THEORY OF IONIZING ATOMIC COLLISIONS
AT THERMAL ENERGIES

By

LAWRENCE RALPH RELYEA

To my parents,

for their constant support,

and to

Linda, Jonathan and Matt,

who, finally, no longer

need to ask:

when can Daddy stay home at night ?

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THEORY OF IONIZING ATOMIC COLLISIONS
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By

LAWRENCE RALPH BELYEA

June 1980

Chairman: D. A. Micha
Major Department: Chemistry

Ionization in low-energy atomic collisions involving
electronically excited species is investigated using
coupled channels and effective Hamiltonian theories for
the heavy particle motion. Within the coupled channels
formulation detailed electron energy distributions are
obtained for the Penning ionization of Ar by He(1s2s,^{3}S);
the structure is interpreted as arising from final channel
heavy particle resonances, and this interpretation
provides new insight into the role of the nuclear dynamics
on electron emission. The Riccati transform of the matrix
Schrödinger equation arising in the coupled channels
theory is solved to obtain cross sections for Penning
ionization over a range of energies, and results were

found to compare well with experiment. The validity of a simplifying decoupling approximation is demonstrated by numerical studies; the agreement between "exact" and decoupled results is excellent over a range of energies, and is independent of heavy particle angular momentum partial wave.

An effective Hamiltonian theory for Penning and associative ionization is formulated using projection operator techniques; an effective potential is obtained for the nuclear motion of a discrete electronic state which is unstable with respect to decay by electron emission. Analysis of a complex, non-local and energy-dependent potential energy kernel demonstrates for the first time that while a local approximation to the real part may be valid, such approximation may not be valid for the imaginary part.

A method is presented for solving inhomogeneous, second-order ordinary differential equations with a complex, non-local kernel, and simplifications for the case of a purely imaginary kernel are discussed.

INTRODUCTION

The interaction of electronically excited atoms and molecules with ground state species is of practical interest in lasers, plasmas and atmospheric chemistry and of theoretical interest for the understanding of energy transfer mechanisms. The subject of this dissertation is the quantum mechanical study of the dynamics and energetics of ionizing collisions in atoms where the nature of the energy transfer is in the form of electronic excitation; in particular, attention is focused on the ionization of a neutral target atom in its ground electronic state by an electronically excited, metastable atom.

In addition to the elastic scattering, various reactive channels or pathways are available depending upon the collision energy, the excitation energy of the metastable atom, and those excitations and ionizations of the target which are allowed by energy conservation considerations. If the metastable atom excitation energy exceeds the ionization potential of the target, ionization can occur; if this excitation is less than the target

ionization energy, excitation and ionization of the target are both possible modes of energy transfer. Final channels (or post-collision rearrangements) will in general then consist of: 1) elastically scattered reactants, 2) de-excited metastable and excited target, 3) de-excited metastable, ionized target plus electron, and 4) molecular ion plus electron.

It is the object of this work to put forth a theory of ionizing collisions of atoms with metastables in the case where the electronic excitation energy of the excited atom exceeds the ionization energy of the target; the processes are referred to as associative or Penning ionization (AI or PI) depending upon whether the heavy particles are bound or unbound, respectively, in the ionized channel. Such a theory should be sufficiently detailed so as to be able to be predictive of some of the wide range of experimental observations which are possible for such a collision process: roughly in order of increasing detail, one may measure total ionization cross section and its energy dependence, branching (AI/PI) ratio and its energy dependence, angular distribution of elastically scattered particles, angular distribution of de-excited metastable and ionized target, vibrational and rotational distributions for AI, and angle- and energy-dependent distributions of the ejected electron. Analysis of results such as these can provide useful insights into

features of both the collision dynamics and the ionization mechanism.

Following a mathematical review, a brief survey of approaches to the collisional ionization problem will be made in Chapter I. To complete the review and anticipate some of the numerical results to be presented later, a recent coupled-channels approach which makes use of a discrete approximation to the electronic continuum will be discussed.

In Chapter II a discussion of the electronic states appropriate to the problem of ionizing heavy-particle collisions will be presented. The construction of proper molecular resonance and continuum electronic states is discussed in some detail. Then the collision problem for nuclei and electrons will be analyzed in terms of a projection operator formalism; given a basis of Born-Oppenheimer electronic states, the space spanned by these states is partitioned in a physically appealing way into a "Q-space" or "bound" portion and a "P-space" or "continuum (scattering)" subspace. Heavy particle motion in the entrance channel (whose state has a zero projection in P) will then be described in terms of a complex, non-local, energy-dependent effective Hamiltonian which accounts for both elastic scattering and ionization. The various transition amplitudes relevant to AI, PI and elastic scattering will be derived, along with the

corresponding scattering cross sections. The computational scheme developed for the solution of the scattering equations in a coupled channels theory will be discussed in Chapter III. Application of the theory for Penning ionization will be made for a particular choice of collision partners, $He^*(1s2s, {}^3S)$ and Ar, and various cross sections and energy distributions will be compared to recent experimental results. Analysis of electron energy distributions is seen to lead to a more refined picture of the Penning "mechanism" in terms of a certain type of heavy-particle resonance.

In Chapter IV we will discuss the solution of an inhomogeneous differential equation describing heavy particle motion for Penning and associative ionization in atomic systems. Various approximations to the real and imaginary parts of the complex, non-local kernel are examined in detail. We will present a method for the solution of inhomogeneous differential equations for such a kernel; the treatment is general, and we comment on its implementation for a particularly useful approximation to the kernel. The chapter concludes with a summary of the present work and a discussion of problems where further study is warranted.

I.1 Separation of Electronic and Nuclear Motion

Our goal lies in the solution of the Schrödinger equation

$$(E - H)\Psi = 0 \qquad (1.1)$$

where H is the Hamiltonian for a system of nuclei and electrons. Inasmuch as this work is devoted to a study of ionizing collisions between atoms, we restrict our treatment in what follows to diatomic systems. We write, for an N-electron system,

$$H = H_{el} + T_R \qquad (1.2)$$

with T_R, the nuclear kinetic energy operator, given by

$$T_R = -(\hbar^2/2M) \, \nabla_R^2 \qquad (1.3)$$

$$M = M_A M_B / (M_A + M_B) \qquad (1.4)$$

where M_A (M_B) is the mass of atom A(B). The electronic Hamiltonian H_{el} is

$$H_{el} = \Sigma(i=1,N) \; \{(-\hbar^2/2m_i) \, \nabla_i^2$$

$$-Z_A e^2/|r_i - r_A| - Z_B e^2/|r_i - r_B| \qquad (1.5)$$

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$$+ \sum(j<i=1,N) \; e^2/|\underset{i}{r} - \underset{j}{r}|\} + Z_A Z_B \; e^2/|\underset{A}{R} - \underset{B}{R}|.$$

The terms are the usual electron kinetic energy and electron-nuclear, electron-electron and nuclear-nuclear interactions. We have neglected both the mass polarization terms which arise from the transformation to center of mass coordinates (Froman, 1962) and spin orbit interactions. The splitting of H (1.2) is done to exploit the mass disparity between electrons and nuclei, in order that we may solve separately for electronic and nuclear motion.

We now introduce a complete and orthonormal set of discrete electronic states $\{\phi_i(\underline{r};R)\}$ where $\underline{r}$ denotes the collection of electronic coordinates, R is the internuclear separation, and i labels a particular state. These states are adiabatic states in the sense that their dependence upon the internuclear coordinate is parametric rather than dynamic. Apart from this restriction, these functions are otherwise unspecified at this point. We merely mention here that this basis must be augmented by continuum electronic states when we wish to study the collisional ionization problem in the next chapter.

Expanding Ψ in this basis (our notation is that of Tully (1976))

$$\Psi(\underline{r},\underline{R}) = \sum(i=1,n) \; \phi_i(\underline{r};R) \, X_i(\underline{R})$$

$$= \sum(i=1,n) \quad \phi_i X_i \tag{1.6}$$

substituting into (1.1), premultiplying by ϕ_j^* and integrating over electronic coordinates yields, for the expansion coefficients (i.e., nuclear wavefunctions),

$$(E - T_R - V_{jj} - T''_{jj}) X_j =$$

$$\sum(i \neq j = 1, n) \quad (V_{ji} + T''_{ji} + T'_{ji}) X_i \tag{1.7}$$

where

$$T''_{ji} = -(\hbar^2/2M) \langle \phi_j | \nabla_R^2 \phi_i \rangle \tag{1.8}$$

$$T'_{ji} = -(\hbar^2/2M) \langle \phi_j | \underline{\nabla}_R \phi_i \rangle \cdot {}^{\circ} \underline{\nabla}_R \tag{1.9}$$

$$V_{ji} = \langle \phi_j | H_{el} | \phi_i \rangle \tag{1.10}$$

and where $\langle ... \rangle$ denotes an integration over electronic coordinates; we have used the fact that for ϕ_i real and orthonormal, the diagonal terms T'_{jj} are identically zero (Dalgarno and McCarroll, 1956; 1957). The diagonal terms V_{jj} are the potential energy surfaces for nuclear motion; the terms T''_{jj} are non-adiabatic corrections to these surfaces. Non-adiabatic interactions are given by the terms T''_{ji} and T'_{ji}. All T'' and T' terms may be collectively thought of as describing the response of the

electrons or of the electronic state to the nuclear motion. The result (1.7) is exact, given the form (1.2) of H and the adiabatic hypothesis.

The mass disparity between electrons and nuclei has as a consequence a qualitative difference between electronic and nuclear motions: electronic motion is comparatively rapid and highly quantized, while the heavy particle motion is considerably slower and more nearly classical. This observation is the essence of the Born-Oppenheimer approximation, which mathematically amounts to neglect of all T" and T' terms in the last result. This gives

$$(E-V_{jj} -T_R) X_j = \Sigma(i \neq j=1,n) V_{ji} X_i . \qquad (1.11)$$

Justification for this step, based upon order-of-magnitude estimates of the quantities involved, may be found in O'Malley (1971). Without further specification of the electronic basis we see that, even in the B-O approximation, transitions among states are possible by the couplings through H_el . With this we have completed our review of the separation of nuclear and electronic motions. We now turn our attention to a discussion of the possible choices for the states {ϕ_i}.

I.2 Representations of Electronic Wavefunctions

We have as yet left unspecified the set of electronic states $\{\phi\}$. There are two classes of representations which have been utilized in descriptions of atomic collision processes; these are the adiabatic representation on the one hand, and a variety of diabatic representations on the other.

The standard adiabatic representation (Smith, 1969) of quantum chemistry is obtained by choosing for the set $\{\phi\}$ those states which are eigenfunctions of H_{el}, i.e.,

$$H_{el}\phi_i = E_i\phi_i ,$$ (1.12)

where

$$E_i(R) = <\phi_i|H_{el}|\phi_i> = V_{ij}\delta_{ij} .$$ (1.13)

The result (1.7) now reads

$$(E - T_R - E_j - T''_j)X_j =$$

$$\Sigma(i \neq j=1,n) \ (T''_{ji} + T'_{ji})X_i .$$ (1.14)

Couplings through H_{el} are absent; the off-diagonal T'' and T' terms are the couplings which account for transitions to other energy surfaces. During a collision process the particles can be thought to move along the resulting adiabatic potential energy surfaces, and transitions take place between states due to the nuclear kinetic energy

operator. In regions where adiabatic surfaces are in
close proximity, the otherwise-small couplings can become
quite large and it is in these regions that there is a
high probability of transition from one state to another.
If we invoke the B-O approximation, we obtain, in analogy
with (1.11),

$$(E - T_R - E_j) X_j = 0 .$$ (1.15)

At this point the states X_j have become completely
uncoupled, so what we have is a representation
corresponding to stationary states of molecules. The
states of the standard adiabatic representation exhibit
another important property, namely that the non-crossing
rule (von Neumann and Wigner, 1929) applies to states of
the same symmetry. This results in "avoided crossings" of
potential energy surfaces, together with large electronic
wavefunction gradients in the vicinity of these points.
Although this description has enjoyed widespread use by
quantum chemists, it is clear that it is wholly unsuitable
for the scattering theorist when considering a reactive
collision problem where the system can no longer be
thought to stay on one PE surface. It is conceivable to
calculate adiabatic energy surfaces and all the B-O
coupling terms using electronic eigenstates and then
transform to a different representation more suited to a
particular collision problem. However, electronic

wavefunctions are usually determined for a few select clamped-nuclei geometries; since these wavefunctions do not have explicit dependence upon the internuclear coordinates, and as these coordinates are actually continuous variables, it is easy to see that this is not a feasible program to carry out. An added consideration is the size of the expansion basis {ϕ} and hence the number of coupled states appearing in (1.6). In a process involving multiple surfaces we usually need to include those states that are "close" to the initial surface, in the sense that they are energetically accessible; we often need to include closed channels (energetically inaccessible states) as well. Hence we are often confronted with the need for excited-state surfaces; these are usually not of the same quality as the lower lying states.

An alternative to this approach is to consider as our electronic basis states which are not eigenstates of H_{el}. This notion dates back as far as Zener (1932), and the term _diabatic_ to describe a state which does not adiabatically adjust to the instantaneous position of the nuclei was coined in comparatively recent times (Lichten, 1963; 1967). It is interesting to note that until this time, the prevalent notion of molecular theorists was that the diagonal states were _the_ electronic states.

Unfortunately, there is no unique set of states which satisfy the requirement of a diabatic representation; they lack general definition. The later work of Smith (1969) was significant in this connection. Smith's representation consisted of choosing the electronic basis in such a manner that the off-diagonal terms T" and T' vanish; in a sense, the Born-Oppenheimer approximation becomes exact in this representation. Variations on this theme have these terms small but not necessarily zero. The reader is directed to the recent work of Delos and Thorson (1979) in this connection. In all such pictures, however, the dominant coupling appears in the V_{ij} terms, the off-diagonal matrix elements of H_{el}. The large gradients found in the adiabatic wavefunctions become small or, in the case of Smith's representation, zero. Diabatic states are not constrained to obey a non-crossing rule and go smoothly through "avoided crossings." The non-crossing rule is thus not a law of nature but appears only as an artifact of a particular choice of representation of the electronic states of molecules.

This completes our survey of the mathematical background. We will now review a few of the theoretical approaches to collisional ionization in the next section.

I.3 Survey of Theories of Collisional Ionization

Ionizing collisions in atoms of the type

$$A* + B --> A + B+ + e-$$
$$--> AB+ + e-$$

where A is electronically excited have been the subject of considerable experimental and theoretical interest as these processes may have large reactive cross sections even at low (thermal) energies. For the case where the electronic excitation energy of A exceeds the ionization potential of B, the initial discrete N-electron electronic state is degenerate with the continuum of electronic states corresponding to the remaining N-1 bound electrons and the free electron. Schematic potential energy curves for N and N-1 particle states are displayed in Figure 1; the lower curve is the threshhold of an electronic continuum. The initial (A*,B) state may thus be thought of as an autoionizing or resonance electronic state. Among the important theoretical aspects of this process are the coupling between discrete and continuum electronic states, the coupling among continuum electronic states, and finally the influence of these coupled states upon the heavy particle dynamics.

Classical treatments (Miller and Schaefer, 1970) are based on a close encounter of metastable and target, with autoionization occurring at the classical turning point (distance of closest approach) in the effective (AB* plus

centrifugal) potential. Further, the kinetic energy of relative motion of A* and B must exceed the maximum in the effective potential for reaction to occur. A slightly more detailed description (Miller, 1970) makes use of an autoionization width γ for decay of the discrete state into the continuum. Transitions may occur at separations greater than the classical turning point, so a transition probability may be obtained for the heavy particles both on the inward and outward parts of their trajectory.

Semiclassically one obtains a probability amplitude (or S-matrix element) as a superposition of probabilities; differential and total cross sections then depend upon the square modulus of the amplitude and so differ from the classical result in that interference terms (arising from interference between transitions during in and out trajectories, for example) are now present.

Since the resonance state lies in the continuum of the ionized channel, quantum mechanical treatments have been based largely upon a complex, local adiabatic potential which governs the heavy particle dynamics (Nakamura, 1969; Miller, 1970; Miller and Schaefer, 1970). This complex potential results in complex phase shifts, and the imaginary part of the potential accounts for loss of flux (via inelastic and/or reactive processes) from the initial channel (Mott and Massey, 1971; Micha, 1974). A formal development involving an effective Hamiltonian

derived using projection operator algebra, and which contains the local, complex potential as an approximation, will be presented in detail in Chapter II. However, at this point we wish to review a recent and novel theoretical approach (Bellum and Micha, 1978) to chemiionization to set the stage for both the developments in Chapter II and a portion of the numerical results to be presented in a subsequent chapter.

For the particular collisional ionization processes we wish to study, Penning and associative ionization, the final ionized channel consists of bound or unbound nuclei plus a free electron. Consequently, an electronic basis consisting solely of discrete (bound) electronic functions is inappropriate here. Since the outgoing electron can have arbitrary kinetic energy (constrained only by conservation of total energy during the collision), we need to augment the discrete basis by a continuum of electronic states $\phi(\epsilon)$; here ϵ labels the asymptotic kinetic energy of the free electron. A prescription for constructing such resonance and continuum electronic states is given in the next chapter. Assuming for the moment that only a single initial discrete state ϕ_d is significant, we expand the total wavefunction for nuclei and electrons (in a body-fixed, center of mass of the nuclei frame, BF-CMN) in the basis $[\phi_d, \{\phi(\epsilon)\}]$:

$$\Psi = \phi_d X_d + \int (0,\inf) \, d\in \phi(\in) X(\in) \; . \tag{1.16}$$

Implicit in the above is a neglect of nuclear and electronic angular momentum coupling and the representation of the outgoing electron by a pure s-wave (a more detailed discussion will be presented in Chapter II). In what follows we shall restrict out attention to PI; some remarks concerning extension of the theory to AI will be made at the conclusion of this section. Substitution into the Schrödinger equation, taking the usual scalar products and making a partial wave expansion for the nuclear motion leads to a continuous set of coupled, second-order ordinary differential equations for the heavy particle functions X_d, $X(\in)$.

To make the problem computationally tractable, Bellum and Micha (1978) introduced a complete, orthonormal basis of discrete functions of the continuum variable $\in$, $\{f_J(\in)\}$. Expanding the continuum coefficients in this set

$$X(\in) = \Sigma(J=1,N) \; f_J(\in) X_J \tag{1.17}$$

and proceeding in the usual manner gives rise to a matrix Schrödinger equation of order $N+1$ describing motion of the heavy particles with angular momentum partial wave L :

$$D^L X^L = U^L X^L \tag{1.18}$$

where

$$(D^L)_{ij} = (d^2/dr^2 + k_i^2 - L(L+1)/R^2)\delta_{ij} \qquad (1.19)$$

for $i,j = 1$ to $N+1$,

$$(U^L)_{11} = (2M/\hbar^2)V_d \qquad (1.20)$$

$$(U^L)_{jj} = (2M/\hbar^2)(V_+ + \epsilon_J) \qquad (1.21)$$

for $j = J+1 = 2$ to $N+1$, and

$$(U^L)_{ij} = (2M/\hbar^2)(\Delta\epsilon)^{1/2}V_{dJ}$$

$$(1.22)$$

for $i=1, j=J+1=2$ to $N+1$ and $j=1, i=J+1=2$ to $N+1$, and zero otherwise. Channel wavenumbers and the reduced mass are given by k_i and M. The potentials V_d and V_+ are diabatic potential energies for the initial discrete state and molecular ion state, respectively. The coupling V_{dJ} is the electronic matrix element between the discrete state and the J-th discretized continuum state; ϵ_J is the kinetic energy of the ejected electron in the J-th interval of the continuum. The choice of the set is that of Bellum and Micha (1978), and is repeated here; for $J = 1, 2, \ldots, N$:

$$f_J(\epsilon) = (\Delta\epsilon)^{-1/2} \qquad (1.23)$$

for

$$\epsilon_J - (\Delta\epsilon)/2 \le \epsilon \le \epsilon_J + (\Delta\epsilon)/2$$

and zero otherwise. An important feature to note is that the couplings between continuum electronic states $(V_{JK}, J \ne K)$ have been neglected. The potential matrix thus blocks as follows:

$$
\begin{bmatrix}
V_d & V_{1d} & V_{2d} & \cdots & V_{rd} & \cdots & V_{Nd} \\
V_{d1} & V_1 + \epsilon_1 & 0 & \cdots & 0 & \cdots & 0 \\
V_{d2} & 0 & V_2 + \epsilon_2 & \cdots & 0 & \cdots & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
V_{dr} & 0 & 0 & \cdots & V_r + \epsilon_r & \cdots & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
V_{dN} & 0 & 0 & \cdots & 0 & \cdots & V_N + \epsilon_N
\end{bmatrix}
\quad (1.24)
$$

The boundary condition for (1.18) at the origin ($R = 0$) reads

$$X^L(0) = 0 \qquad (1.25)$$

and from the asymptotic behavior of the wavefunction we obtain the real and symmetric reaction matrix K (or R matrix) :

$$\lim_{R \to \infty} X^L = J^L + N^L K^L \qquad (1.26)$$

where J and N are diagonal matrices of Riccati Bessel functions of the first and second kind (Abramowitz and Stegun, 1972)

$$(J^L)_{ij} = \delta_{ij} \, k_j^{-1/2} \, J_L(k_j \, R) \tag{1.27}$$

$$(N^L)_{ij} = \delta_{ij} \, k_j^{-1/2} \, N_L(k_j \, R). \tag{1.28}$$

Recall that we have restricted our treatment to PI, so only open channels ($k_j^2 > 0$) of nuclear motion are considered. The unitary and symmetric scattering matrix S is given in terms of K (Mott and Massey, 1971) by

$$S^L = (1 + iK^L)(1 - iK^L)^{-1} \tag{1.29}$$

The obvious advantage to using K matrix boundary conditions is that we may work entirely with real quantities, rather than the complex functions dictated by S matrix boundary conditions. Within the above treatment, the partial wave reactive scattering amplitude is

$$S^L_{C1}(E) = \Sigma(J=1,N) \, f_J(\epsilon) \, S^L_{J1}(E) \tag{1.30}$$

where the S^L_{J1} are amplitudes for collision with emission of an electron with kinetic energy distribution given by the probability amplitude $f_J(\epsilon)$. The Penning ionization cross section per unit energy of the emitted electron (also known as Penning Electron Energy Distribution or PEED) is thus

$$d\sigma(E,\epsilon)/d\epsilon = \pi/k_d^2 \; (\Delta\epsilon)^{-1}$$

$$* \Sigma(L) \; (2L+1) \; |S(E)|^2_{J1}$$

$$(1.31)$$

and the Penning ionization cross section is given by

$$\sigma(E) = \int(0,\epsilon') \; d\epsilon \; d\sigma(E,\epsilon)/d\epsilon \qquad (1.32)$$

where ϵ' is the maximum value of the emitted-electron kinetic energy for PI and is fixed by energy conservation once the initial collision energy is specified.

In the previous work (Bellum and Micha, 1978) the neglect of the continuum-continuum couplings suggested the following approximation: replace the $N+1$ - dimensional matrix problem by N 2-state problems (in essence, each discrete-continuum transition is taken to be independent of all others), namely

$$D^L_J \; Y^L_J = U^L_J \; Y^L_J \qquad (1.33)$$

where we explicitly write $(\hbar^2/2M)U^L_J$ as

$$\begin{bmatrix} V_d & (\Delta\epsilon)^{1/2} V_{dJ} \\ (\Delta\epsilon)^{1/2} V_{dJ} & V_+ + \epsilon_J \end{bmatrix} \qquad (1.34)$$

for $J=1$ to N. We will examine in detail (by way of numerical studies) the validity of this decoupling approximation in a later chapter, and in particular will

focus on the cross sections (1.31) and (1.32) resulting from the full matrix problem and from the N 2-state problems. In view of the anticipated reduction in computational effort in solving N pairs of coupled second order, ordinary differential equations versus a matrix differential equation of order N+1, it is critical to have knowledge of the range of applicability of this approximation; this has implications for both this and other coupled channels treatments of PI (including recent work on PI in a laser field: Bellum and George, 1978; 1979; Bellum, Lam and George, 1978)).

When we wish to extend the coupled channels theory to the case of associative ionization, where the heavy particles remain bound after electron emission, we discover at once that the boundary conditions of this problem are such as to complicate the solution. For closed channels, $k_j^2 < 0$ and the matrix elements of J and N are given in terms of modified spherical Bessel functions of the first and third kinds (Abramowitz and Stegun, 1972)

$$(J^L)_{ij} = \delta_{ij} (k_j R)^{1/2} I_{L+1/2} (k_j R) \qquad (1.35)$$

$$(N^L)_{ij} = \delta_{ij} (k_j R)^{1/2} K_{L+1/2} (k_j R). \qquad (1.36)$$

The K matrix then blocks as follows :

$$
\begin{bmatrix}
K_{oo} & K_{oc} \\
K_{co} & K_{cc}
\end{bmatrix}
\qquad (1.37)
$$

where K_{oo}, K_{oc}, K_{co} and K_{cc} are the open-open, open-closed, closed-open and closed-closed sub-matrices of K. The S matrix is then expressed in terms of K_{oo} in analogy with (1.29). However, the modified Bessel function $K_{L+1/2}$ pertaining to closed channels exhibits exponentially decreasing behavior with increasing R, and we realize that there will be numerical difficulties in trying to extract the amplitude of this decaying component.

Apart from this obstacle which precludes extension of this coupled channels methodology to AI, there are other problems of a fundamental nature when one attempts to apply the discretization concept in a general case. One difficulty is to reconcile the general notion of a discretization of the electronic continuum with the fact that the final nuclear states in AI are discrete (i.e., the vibration-rotation levels of a molecular ion). In other words, a portion of a discretization basis ought to span the discrete part of the electron kinetic energy range (corresponding to AI) as well as the continuum part

(corresponding to PI). This suggests that we need to know in advance the detailed vibrational-rotational structure of the molecular ion. In PI, the same discretization basis was used for each heavy particle angular momentum partial wave. By contrast, for AI the basis would need to be different for each partial wave: a different set of vibrational levels (with different level spacings) is accessible for each L value. Furthermore, if we wished to generalize the preceding model to include higher angular momentum partial waves for the emitted electron, this may introduce yet another angular momentum dependence of a discretization basis set. One last aspect of this problem is the functional form of the discretization basis; the set of functions of Bellum and Micha (1978) and used by Relyea and Micha (1979) was chosen on physically appealing grounds. For a more general choice of basis (e.g., overlapping functions) the potential matrix U does not block as in (1.24) and the possibility of invoking an analogous (and expedient) decoupling approximation may be lost.

Although the numerical study suggested by the above remarks is beyond the scope and intent of the present work, a final assessment of this theory must await numerical experiments as regards discretization basis set type and size, as well as an examination of the validity of other approximations that have been made. The

computational scheme for the solution of the PI part of the collisional ionization problem will be presented in Chapter III, together with detailed results pertinent to the Penning ionization of Ar by He*(1s2s,^{3}S) at thermal energies.

In the next chapter we will present an alternative approach to the coupled channels treatment described in this section. It is an effective Hamiltonian theory based upon projection operator techniques, and we will see that many of the deficiencies of the coupled channels method are remedied in the new theory. In a later chapter we propose methods of solution of the resulting scattering equations at various levels of approximation.

Figure 1 Potential Energy Curves for PI and AI

POTENTIALS FOR PI AND AI

U (AND. UNITS) [×10⁻³]

R (BOHR)

A* + B

A + B⁺
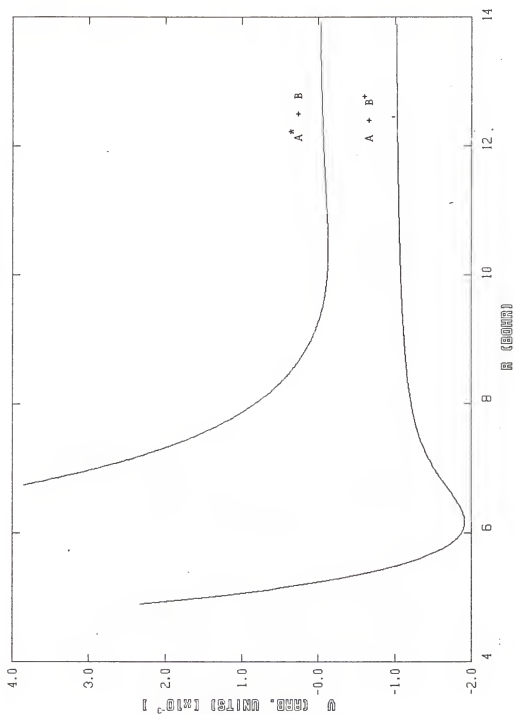
INEN, McIntosh Plot System - Mexico   16/03/80   23.11.00

CHAPTER II
EFFECTIVE HAMILTONIAN FORMALISM FOR
IONIZING ATOMIC COLLISIONS

II.1 Electronic Wavefunctions Appropriate to Penning and Associative Ionization

Before proceeding to develop a theory for the heavy particle dynamics of collisional ionization in atomic systems, consideration must first be given to the electronic wavefunctions appropriate to such processes. Once a prescription has been given for the construction of electronic wavefunctions for the initial AB* and final (AB+,e−) states, potential energy functions and couplings may then be used in a theory of heavy particle dynamics.

As has been already mentioned in the preceding chapter, the initial discrete electronic state of AB* is embedded in a continuum of states of the type (AB+,e−) and as such is an autoionizing electronic state, capable of decay by electron emission even in the limit of zero relative velocity of the nuclei. Interpreted as a molecular autoionization for fixed nuclei, the transition rate would be independent of the B-O couplings which dynamically couple electronic and nuclear motions. This transition will be governed by a coupling, through an electronic Hamiltonian, of the (as yet unspecified) discrete and continuum electronic states; for the low

energy collisions to be considered in this work it is reasonable to assume that such couplings still dominate the process. These remarks suggest that we must construct a diabatic (non-diagonal) representation of the electronic Hamiltonian; we will now review some conventional techniques for obtaining such wavefunctions with particular attention to the description of the continuum electronic state.

Following the historical development where the application first was to three—electron systems (He* + H), Miller et al. (1972) chose to represent both the initial discrete function ϕ_i and the molecular ion function ϕ_+ by configuration interaction (CI) wavefunctions. For ϕ_i this is an application of the "stabilization" method of Hazi and Taylor (1970). It has long been argued that although autoionizing or resonance states are not true electronic eigenfunctions (in that they require some constraint for their definition), they can still be obtained by the established procedures for calculating ordinary bound states: one looks for a positive energy root which is stable with respect to basis set change and identifies such a state as a resonance or "bound state in the continuum." A continuum electronic state is constructed by augmenting the determinants in ϕ_+ by a continuum orbital

of energy ϵ; this form ensures a properly antisymmetrized continuum electronic state. For the continuum orbital a Coulomb orbital centered on the hydrogen atom and orthogonalized to all the bound MO's was employed. A Coulomb orbital is a reasonable description for an electron outside of an ionic core; the effect of distortion at shorter distances is neglected. The autoionization width is given by

$$\gamma = 2\pi\rho \, |<\phi(\vec{\epsilon};1,2,..,N)\,|H_{el}\,-E_i|\phi_{}(1,2,..,N)>|^2 \qquad (2.1)$$

where ρ is the density of final states and H_{el} the electronic Hamiltonian. The wavefunction $\phi(\vec{\epsilon};1,2,..,N)$ is a continuum function in which the free electron has energy ϵ and orientation $\hat{\epsilon}$ in the body-fixed frame. It was in anticipation of the width calculation that the same set of MO's was used for both ϕ_i and ϕ_{+}; this eliminated the need for taking matrix elements between determinants containing non-orthogonal orbitals. Bound-free matrix elements were evaluated numerically. Technical details aside, this approach ensures the orthogonality of bound and continuum states and guarantees that the continuum state obeys the boundary condition appropriate to a scattering (positive energy) state at large distances.

A more recent formulation (Hickman et al., 1977), again for He* + H, represented the molecular ion state ϕ_{+}

by a single determinant and constructed N-electron states
by

$$\phi_m (1,2,\ldots,N) = A\{\phi_+ (1,2,\ldots,N-1) u_m (N)\} \quad (2.2)$$

where $\{u_m\}$ is some MO basis and A is the antisymmetrizer.
These new states have the physical form of an ionic core
plus another orbital; they are not continuum states.
Defining a projection operator P by

$$P = \sum(m=1,M) |\phi_m (1,2,\ldots,N) >< \phi_m (1,2,\ldots,N)| \quad (2.3)$$

they diagonalized $(1-P) H_{el} (1-P)$ in some multi-determinantal
basis (CI) to extract those bound states orthogonal to
states in the P subspace. The ground state of HeH was not
one of the eigenvalues of QHQ and was obtained by
diagonalizing the full electronic Hamiltonian. All states
of QHQ were thus autoionizing or resonance states of
positive energy; the desired eigenvalue was the lowest
root of QHQ. The resonance state energies were
essentially identical with those obtained from the
stabilization technique applied to the full H_{el},
demonstrating the advantage to diagonalizing only a
sub-block if a prudent choice of P is made. It also
appears that one key to the success of this method is to
include enough configurations in P so that the resonance
is the lowest solution of QHQ but yet to leave Q "large

enough" to give an accurate resonance function. A continuum wavefunction $\phi(\vec{e};1,2,\dots,N)$ was constructed as

$$\phi(\vec{e};1,2,\dots,N) = A\{\phi_+(1,2,\dots,N-1)\phi(\vec{e};N)\} \quad (2.4)$$

where $\phi(\vec{e};N)$ is a Coulomb orbital orthogonalized to the ϕ_+ orbitals. An important aspect of this work was the neglect of the non-square-integrable portion of the orthogonalized Coulomb orbital. Justification for this procedure was found in the fact that for a set of MO's which is a good basis in a localized region in space, the continuum part of this orthogonalized continuum orbital will be large only outside this region. Since the dominant contribution to the autoionization width came from the inner region, this neglect did not constitute a severe numerical error. Although computationally expedient, the "continuum" state thus obtained now obeys boundary conditions appropriate to bound-state wavefunctions, namely asymptotic decay. Further, the resonance and continuum electronic states were orthogonal only because the same MO basis was used in the construction of ϕ_i, ϕ_+ and $\phi(\vec{e};N)$.

Another scheme for obtaining autoionizing or resonance states of molecules is the calculation of so-called Siegert eigenvalues (Siegert, 1939); in more recent applications (Bardsley and Junker, 1972; Isaacson, 1979; Isaacson and Miller, 1979; McCurdy and Rescigno,

1979) orbital basis sets for CI are augmented by complex
orbitals asymptotically representing Coulomb orbitals, and
the resulting complex Hamiltonian matrix is diagonalized
to obtain eigenvalues and vectors. Applications of any of
the above techniques, capable of producing very high
quality electronic wavefunctions and ionization widths,
are in practice limited to few-electron systems; treatment
of larger systems at the Hartree-Fock or post-HF level is
ordinarily facilitated by using atomic core
pseudopotentials, restricting excitations when
constructing CI determinants, etc.

For the ionization of Ar by He*(1s2s,^{3}S) we will need
an electronic wavefunction for (or the potential
corresponding to) the initial $^3\Sigma$ state; for the final
channel molecular ion state which separates to He +
Ar$^+$(^{2}P) we would in principle need both $^2\Sigma$ and $^2\pi$ states.
As our ultimate interest will be in collision energies on
the order of 0.1 eV, we may safely neglect additional
states in either channel. The closest-lying state of
higher energy for HeAr* corresponds to He(1s2p,^{3}P) + Ar
and lies (asymptotically) over 1 eV (Moore, 1949) above
the initial state; an excited state of HeAr$^+$ corresponding
to He + Ar$^+$(3s^{1}3p^6,^{2}S) lies over 13 eV above He +
Ar$^+$(3s^{2}3p^5,^{2}P).

Assuming the projection of electronic orbital angular
momentum is conserved in the collision process, we

conclude that the emitted electrons are in either σ or π orbitals. However, recent experimental evidence (Hoffman and Morgner, 1979) lends strong support to the idea that only σ electrons are emitted; i.e., HeAr$^+$ is formed only in the $^2\Sigma$ state. This may at first be surprising in that the statistical weights for forming $^2\Sigma$ and $^2\pi$ are in the ratio of 1:2 in collisions of He and Ar$^+$. However, we must bear in mind that in PI and AI the molecular ion is formed not by collision of He and Ar$^+$ but by decay of HeAr* by electron emission. On the basis of the preceding remarks we are justified in treating the heavy particle dynamics as a two-state process: a $^3\Sigma$ state for the initial channel and a $^2\Sigma$ state for the molecular ion channel.

For the initial "hole" state ($^3\Sigma$), inspection of separated-atom energies of He, He*, Ar and Ar$^+$ (Moore, 1949) indicates that it is not the lowest energy state of that symmetry; for the open-shell ion, HeAr$^+$ ($^2\Sigma$) is the lowest state of its symmetry. For recent results on HeAr$^+$ the reader is directed to the work (SCF, CI) of Olson and Liu (1978) and to the SCF results of Sidis et al. (1977). Although no ab-initio results are available for HeAr*, a one-electron model has recently been developed by Siska (1979a). Results for both systems at the MSX$_\alpha$ level have been previously reported by Bellum and Micha (1974; 1977). Our effort does not focus just on obtaining initial or molecular-ion wavefunctions of arbitrary accuracy but

rather is directed at using such results to obtain wavefunctions and potentials appropriate to collisional ionization processes. Our requirements on the wavefunctions are 1) that the discrete and continuum states are orthogonal (recall our close-coupling expansion in Chapter I was in terms of an orthogonal basis) and 2) that we have a realistic description of the continuum orbital, since in low-energy collisional ionization "slow" electrons are ejected, and these will have interaction with the ionic core which deviates from Coulombic at short distances.

The major difficulty in obtaining a proper description of a continuum state is in the representation of the outgoing electron. For very high energy electrons a plane wave (PW) or orthogonalized plane wave (OPW) treatment is often adequate. At lower energies Coulomb wave (CW) or orthogonalized Coulomb wave (OCW) are better descriptions as they represent the true field experienced by the electron at large distances from the ion. These approaches all share the same defect: an assumption for the form of the free electron wavefunction. Since this orbital represents a scattering state it is perhaps more natural to approach its description using the tools of scattering theory, although for collisional ionization this approach seems to have been overlooked. Simply stated, we could attempt to solve the problem of the

scattering of a low-energy electron by an open shell molecular ion. Indeed, in the fixed-nuclei approximation a formulation has been given for electron scattering by closed shell, neutral targets by Burke and Sinfailam (1970) (in the static exchange approximation) and by Chandra and Temkin (1976) (for a static plus model polarization potential). Thus the tools are available for the construction of reliable potentials with which to solve the electron-molecule (and maybe molecular ion) scattering problem. However, this constitutes a rather ambitious undertaking and we would prefer to utilize traditional bound state techniques to improve upon and extend the work discussed at the beginning of this section.

We now briefly outline a scheme whereby the wavefunctions (whose matrix elements are the desired potentials) may be constructed.

1) First obtain a molecular ion wavefunction $\phi_+ (1,2,\ldots,N-1)$ for the open shell ($^2\Sigma$) state which asymptotically correlates with He + $Ar^+(^2P)$. As it is the lowest of Σ symmetry it is likely to be obtainable by variational means, although a post-HF method may be needed to ensure correct dissociation.

2) To go beyond the Coulomb approximation for the emitted electron a straightforward approach is proposed

here. We choose to adopt the method of Harris (1967) which has been applied extensively to atomic problems. First we obtain a wavefunction for the molecular ion $HeAr^+$ at the HF level. In general the solution will yield both bound (negative energy) and virtual (unoccupied) molecular orbitals. The virtual orbitals are not stationary (except in special circumstances) with respect to basis set variation as they do not correspond to bound electronic states. These orbitals can be thought of as providing a representation for the scattering of an electron by $HeAr^+$ in its $^2\Sigma$ state. A continuum electron orbital can be expanded in a L^2 basis augmented by regular and irregular non-L^2 functions which properly account for scattering boundary conditions; a purely L^2 expansion can only provide a good description of a scattering function in a localized or truncated region of space and does not satisfy correct boundary conditions. For an electron outside a neutral atom or molecule these scattering functions could be regular and irregular spherical Bessel functions; for a molecular ion the proper choice would be Coulomb functions. Application of the Harris method proceeds as follows: at incident electron kinetic energies equal to each of the positive virtual orbital energies and for the choice of the HF orbitals as the L^2 basis, the ratio of the amplitudes of the non-L^2 functions is obtained, and this defines the scattering orbital

wavefunction. Modifying the computational basis yields a new set of virtual orbitals with new energies, and repeating the above procedure we can generate a collection of continuum orbitals at practically any energy. This treatment is often termed a static-exchange treatment; strictly speaking, exchange is really only included in the target wavefunction. To explicitly include exchange effects between the incident electron and the target requires antisymmetrization of the total electronic wavefunction; this effect can be less rigorously included by addition of an approximate exchange potential in lieu of antisymmetrization. Effects of polarization of the molecular ion by the free electron can also be included by model polarization potentials. Approximations to exchange and polarization contributions are common techniques in current electron-molecule coupled channel calculations. We can now construct a collection of continuum electronic wavefunctions of the form

$$\phi(\vec{\epsilon};1,2,\ldots,N) = [\phi_+(1,2,\ldots,N-1)\phi(\vec{\epsilon};N)]$$

where $\phi(\vec{\epsilon};N)$ is the scattered orbital; $\vec{\epsilon}$ represents the orientation $\hat{\epsilon}$ and magnitude ϵ of the emitted electron energy in the body-fixed frame.

3) To obtain the molecular resonance state we could first calculate a HF ground state $\phi^0(1,2,\ldots,N)$ for HeAr ($^1\Sigma$). A zeroth order approximation to the hole state

ϕ^0_{hs} (1,2,...,N) could be obtained by a particular single

excitation out of ϕ^0. This wavefunction is then

orthogonalized to the continuum wavefunctions obtained in

2) to give a crude description of the molecular resonance,

ϕ_r. An improved treatment could be obtained by

constructing a projector P in the continuum function space

of 2) and solving the CI problem for $(1-P)H(1-P)$. The

basis could be the orbitals of ϕ^0_{hs}.

The above scheme yields wavefunctions which satisfy

the requirements of a diabatic representation: since

neither resonance nor continuum states are eigenfunctions

of the full electronic Hamiltonian, they will have

non-zero matrix elements with H_{el}. It also satisfies our

two previously stated requirements on the continuum

wavefunction: orthogonality to the resonance state and an

improved description of the outgoing electron. It is

hoped that the remarks here may provide stimulation and

motivation to determine quantities of interest in

scattering theory. For diatomic systems of reasonably

light atoms where detailed dynamical studies are possible,

accurate potentials and couplings are desirable since then

an accurate assessment of the scattering theory may be

made.

II.2 Effective Hamiltonian Formalism

With electronic states obtained (in principle) using the methods of the previous section, we will now formulate the heavy particle scattering problem to which these states are needed input. Based upon the remarks in Section I.3 such a reformulation is necessary if the theory is to be able to describe both Penning and associative ionization processes. The methods of Feshbach's unified theory of nuclear reactions (1958, 1962) will be applied to the problem of ionizing collisions; the method of projection operators allows the many-channel (infinite in number in the present work) problem to be recast in terms of an effective Hamiltonian for one of the channels of interest.

The input to our treatment consists of a set of Born-Oppenheimer electronic states; one of these is a discrete state ϕ_d which corresponds to the molecular resonance state of the previous section, and which correlates asymptotically with separated-atom limits of A* + B. In light of the anticipated application we will have a single continuum of electronic states $\{\phi(\vec{e})\}$ associated with a particular state of the molecular ion AB⁺ and which correlates asymptotically with the limits of A + B⁺ + e⁻; here $\vec{e}$ denotes both magnitude ϵ and orientation $\hat{e}$ of the electron in the body-fixed frame. Additional AB⁺

electronic states give rise to multiple continua, each having a different lower limit or threshhold; the theory is generalizable to this situation but the development here will focus on the one discrete - one continuum case. The only restrictions upon the electronic basis $[\phi_d, \{\phi(\vec{e})\}]$ are the orthogonality and normalization conditions

$$\langle \phi_d \mid \phi_d \rangle = 1 \qquad (2.5)$$

$$\langle \phi_d \mid \phi(\vec{e}) \rangle = 0 \qquad (2.6)$$

$$\langle \phi(\vec{e}') \mid \phi(\vec{e}) \rangle = \delta(\vec{e}'-\vec{e}) \ . \qquad (2.7)$$

Since in the present work we are interested in elucidating the effects of nuclear motion on electron emission, the viewpoint is fundamentally different from that of Nakamura (1969; 1971) and Fujii et al. (1970), where Fano's method (1961) for autoionizing atomic states was extended to molecular problems. In these works a totally adiabatic framework was chosen; configuration interaction of discrete and continuum electronic states resulted in a level shift and width for the resonance energy. This energy is necessarily a local quantity since the theory was based upon a fixed-nuclei description of the ionization. This complex resonance energy was then used as the potential for nuclear motion; decay of the initial state by electron emission was governed by the

local, imaginary part of the potential. The theory yielded easily obtainable ionization cross sections but is incapable of providing insights into the interplay of electronic and nuclear motion which is of interest here.

Our method is to construct an operator which governs heavy particle motion in the incident (A* + B) channel and which incorporates effects due to both direct (elastic) and reactive (ionizing) collisions. To accomplish this a projection operator Q is defined onto the molecular resonance state:

$$Q = |\phi_d ><\phi_d| . \tag{2.8}$$

As defined here Q projects only onto the space of electronic wavefunctions and has as a consequence only a parametric dependence upon the internuclear coordinate R. Our choice of Q is similar to that of O'Malley (1966) in a study of dissociative attachment, where a projector was chosen onto the closed electronic channels. The Q channel, although closed with respect to electronic motion, is an open channel for the nuclei. The operator Q, together with its complement P

$$P = 1 - Q \tag{2.9}$$

are the basis for the effective Hamiltonian formalism to be presented here. To the extent that other electronic states can be neglected, P becomes simply

$$P = \int (0,\inf) d\vec{e} |\phi(\vec{e}) ><\phi(\vec{e})| \tag{2.10}$$

which implies nothing more than that the electronic basis constitutes a complete set for our purposes. The Schrödinger equation partitions as

$$Q(E-H)Q\Psi_Q = QHP\Psi_Q \qquad (2.11)$$

$$P(E-H)P\Psi_Q = PHQ\Psi_Q \qquad (2.12)$$

where we have used Q as a subindex on the wavefunction to denote that the initial channel is in the Q subspace; here H is the full Hamiltonian. We also introduce solutions to the corresponding homogeneous equations

$$Q(E-H)Q\Psi_q = 0 \qquad (2.13)$$

$$P(E-H)P\Psi_p = 0 . \qquad (2.14)$$

With the initial channel as Q, the formal solution is given by

$$P\Psi_Q^+ = G_P^+ PHQ\Psi_Q^+ \qquad (2.15)$$

$$Q\Psi_Q^+ = Q\Psi_q^+ + G_Q^+ QHP\Psi_Q^+$$

$$= Q\Psi_q^+ + G_Q^+ QHPG_P^+ PHQ\Psi_Q^+$$

$$= Q\Psi_q^+ + G_Q^+ F^+ Q\Psi_Q^+ \qquad (2.16)$$

where

$$F^+ = QHPG_P^+ PHQ \qquad (2.17)$$

and the reduced Green's functions are

$$G_Q^+ = [Q(E^+ - H)Q]^{-1} \qquad (2.18)$$

and

$$G^+ = [P(E^+ - H)P]^{-1} \; . \qquad (2.19)$$

The effective Hamiltonian for initial channel motion is obtained by noting that for H given by (1.2) and for the choice of Q, the Q-space projection of the total scattering wavefunction for nuclei and electrons is

$$Q\Psi^+ = |\phi_d><\phi_d|\Psi_Q^+>$$

$$= |\phi_d>|X_Q^+> \qquad (2.20)$$

and then

$$(E - V_d - T_R - <\phi_d|F^+|\phi_d>)|X_Q^+>=0 \qquad (2.21)$$

where

$$V_d = <\phi_d|H_{el}|\phi_d> \; . \qquad (2.22)$$

The physical content of (2.21) is the following: the interaction of A* with B is given by the potential V_d; this potential accounts only for elastic scattering in this channel and does not allow for inelastic or reactive processes. The term $<\phi_d|F^+|\phi_d>$ is responsible for ionization through the coupling

$$PHQ = \int d\vec{e}|\phi(\vec{e})><\phi(\vec{e})|H_{el}|\phi_d><\phi_d| \qquad (2.23)$$

followed by propagation in the ionized (AB$^+$,e$^-$) channel governed by G_p^+ and then possible transition through QHP

back to the initial $A^* + B$ state. The heavy particle motion in the initial channel is thus governed by an "optical" potential V

$$V = V_d + <\phi_d |F^+|\phi_d >$$

(2.24)

whose components give rise to direct and reactive scattering. It is clear from (2.17) and (2.19) that the potential is complex and energy dependent. For a discussion of effective Hamiltonians for molecular collisions the reader is directed to the work of Micha (1969; 1974; 1976) and the review of Rabitz (1976). From this point forward our treatment departs from that of Feshbach (1958; 1962) and it is worthwhile to point out the distinction in this work. Following Feshbach we rewrite the second term in V as

$$<\phi_d |QHP[P(E^+ - H)P]^{-1}PHQ|\phi_d >$$

(2.25)

and note that the magnitude of this term will vary rapidly when E is in the neighborhood of an eigenvalue of PHP. Assuming for the moment a set of discrete eigenstates $\{X_i\}$ of PHP, with eigenvalues $\{E_i\}$, we write $(\phi=\phi_d)$

$$V=V_d + \Sigma(i\neq j)<\phi|QHP|X_i >(E^+-E_i)^{-1}<X_i |PHQ|\phi>$$

$$+ <\phi|QHP|X_j >(E^+-E_j)^{-1}<X_j |PHQ|\phi>$$

(2.26)

where E_j is an eigenvalue of PHP in the vicinity of E. For

a given E we have written V as a sum of three contributions, the first two of which presumably vary slowly with E and which give rise to a smooth E-dependence of the cross section; for E near E_j we would anticipate a large contribution to the cross section, a phenomenon which is loosely given the term "resonance." The foregoing remarks have been applied to a single, isolated resonance and must be modified (Feshbach, 1958; 1962; Lemmer, 1966) when there are several eigenvalues (isolated or overlapping) of PHP in the vicinity of E.

For our application the splitting of the optical potential V does not offer any practical advantage. The initial state in PI and AI is itself a resonance (of a different kind). That the initial channel energy may coincide with an eigenvalue of PHP is of secondary importance since resonances of the type illustrated in the Feshbach treatment have not been observed in PI or AI (a different kind of resonance behavior has been uncovered in PEED using the model of Section I.3, and further discussion of such will be deferred until Chapter III).

For our choice (2.10) of P we obtain

$$G^+_P = \int d\vec{e} \int d\vec{e}\,' |\phi(\vec{e}) > g^+(\vec{e}, \vec{e}\,') < \phi(\vec{e}\,')| \tag{2.27}$$

and

$$F^+ = \int d\vec{e} \int d\vec{e}\,' \; V_{d\vec{e}} \, g^+(\vec{e}, \vec{e}\,') \, V_{\vec{e}\,'d} \tag{2.28}$$

where

$$g^+(\vec{\epsilon},\vec{\epsilon}\,') = \langle \phi(\vec{\epsilon}) | \{E^+ - H_{el} - T_R\}^{-1} | \phi(\vec{\epsilon}\,') \rangle \qquad (2.29)$$

and

$$V_{d\vec{\epsilon}} = \langle \phi_d | H_{el} | \phi(\vec{\epsilon}) \rangle \ . \qquad (2.30)$$

The operator g^+ is an operator in the space of heavy particle functions. At this point we introduce two approximations which together will considerably simplify the operators G^+ and F^+_P: assume that 1) we have an approximately diagonal representation of H_{el} within the P subspace, and 2) the continuum electronic energy is that of the N-1 particle state plus the asymptotic energy ϵ of the outgoing electron; we have

$$\langle \phi(\vec{\epsilon}\,') | H_{el} | \phi(\vec{\epsilon}) \rangle = (V_+ + \epsilon) \delta(\vec{\epsilon}\,' - \vec{\epsilon}) \qquad (2.31)$$

where

$$V_+ = \langle \phi_+(1,2,..,N-1) | H_{el}(1,2,..,N-1) | \phi_+(1,2,..,N-1) \rangle \qquad (2.32)$$

and ϕ_+ a molecular-ion wavefunction. This approximation was employed by Bellum and Micha (1978) to render the matrix second-order differential equation more computationally tractable; recall that the decoupling approximation (Section I.3) immediately followed this step. We note here that such further approximation (decoupling) will not be needed in the present

formulation; this will become evident in Chapter IV. Physically, the neglect of continuum-continuum couplings (2.31) stems from the fact that the ejected electron leaves the region of the molecule rapidly compared to the heavy particle relative velocity; there is little likelihood of transitions between continuum states corresponding to different electron kinetic energies. With this we have the diagonal forms

$$G^+_{P,d} = \int d\vec{\epsilon} \; |\phi(\vec{\epsilon})\rangle g^+(\epsilon) \langle\phi(\vec{\epsilon})|$$ (2.33)

and

$$F^+_d = \int d\vec{\epsilon} \; V_{d\vec{\epsilon}} g^+(\epsilon) V_{\vec{\epsilon}d}$$ (2.34)

and where

$$g^+(\epsilon) = \{E^+ - T_R - (V_+ + \epsilon)\}^{-1}.$$ (2.35)

We thus obtain an inhomogeneous differential equation for the Q projection of the total scattering wavefunction

$$\{E - V_d(R) - T_{R_Q}\} X^+(\vec{E}, \vec{R}) =$$

$$\int d\vec{R}' \int d\vec{\epsilon} \; V_{d\vec{\epsilon}}(R) \langle\vec{R}|g^+(\epsilon)|\vec{R}'\rangle V_{\vec{\epsilon}d}(R') X^+_Q(\vec{E}, \vec{R}')$$ (2.36)

where we have assumed spherical symmetry of the initial channel potential V_d and of the coupling $V_{d\vec{\epsilon}}$. To proceed with the analysis we will formally expand $g^+(\epsilon)$ in its spectrum of bound and continuum heavy particle states. As we may ultimately wish to focus separately on either Penning or associative ionization we will treat each of

these cases in turn.

For PI introduce a complete set of heavy particle functions in the ionized channel

$$1_{PI} = \int d\vec{E}' \; |\Psi(\vec{E}')\rangle\langle\Psi(\vec{E}')| \tag{2.37}$$

($E' > 0$ and continuous) where

$$(E'-T_R -V_+)|\Psi(\vec{E}')\rangle = 0 \tag{2.38}$$

and where 1_{PI} denotes the unit operator in this subspace of the total heavy particle function space. Making a partial wave expansion

$$\Psi(\vec{E}',\vec{R}) = \Sigma(l,m) \; Y^*_{lm}(\hat{E}') Y_{lm}(\hat{R}) i^l$$

$$*\exp(i\delta_l)\Psi_l(E',R)/R \tag{2.39}$$

we obtain

$$\langle\vec{R}|g^+(\epsilon)|\vec{R}'\rangle_{PI} = 1/(RR')\Sigma(l,m) \int dE' \; Y_{lm}(\hat{R})$$

$$*Y^*_{lm}(\hat{R}') \Psi_l(E',R)\Psi^*_l(E',R')$$

$$*\{E^+ - \epsilon -E'\}^{-1} \tag{2.40}$$

where the functions $\Psi_l(E',R)$ satisfy the radial equation

$$\{d^2/dR^2 + (2M/\hbar^2)(E'-V_+(R))-l(l+1)/R^2\}\Psi_l(E',R)$$

$$= 0 \tag{2.41}$$

subject to the asymptotic boundary condition

$$\lim_{R\to\infty} \Psi_l(E',R) = A(k')\sin(k'R-l\pi/2 + \delta_l) \tag{2.42}$$

where δ_l is the real partial wave phase shift and $A(k) = k^{-3/2}2\pi^{-1/2}$.

For AI introduce the complete set of bound heavy particle states

$$1_{AI} = \sum(nJN) \; |\Psi_J^{Nn}(E_J^n)><\Psi_J^{Nn}(E_J^n)| \qquad (2.43)$$

$(E_J^n < 0$ and discrete) where

$$(E_J^n - T_R - V_+)|\Psi_J^{Nn}(E_J^n)> = 0 \; . \qquad (2.44)$$

Expanding in partial waves

$$\Psi_J^{Nn}(E_J^n,\vec{R}) = Y_{JN}(\hat{R})\Psi_J^n(E_J^n,R)/R \qquad (2.45)$$

we obtain

$$<\vec{R}|g^+(\epsilon)|\vec{R'}>_{AI} = 1/(RR')\sum(n,J,N) \; Y_{JN}(\hat{R})$$

$$*Y_{JN}^*(\hat{R'}) \; \Psi_J^n(E_J^n,R)\Psi_J^n(E_J^n,R')^*$$

$$*[E^+ - \epsilon - E_J^n]^{-1} \qquad (2.46)$$

where the functions $\Psi_J^n(E_J^n,R)$ are solutions to the vibration-rotation eigenvalue equation

$$\{d^2/dR^2 - (2M/\hbar^2)V_+(R) - J(J+1)/R^2\}\Psi_J^n(E_J^n,R)$$

$$= (2M/\hbar^2) \, E_J^n \, \Psi_J^n (E_J^n, R) \; . \tag{2.47}$$

Making a partial wave expansion of the initial channel heavy particle function X^+_Q

$$X^+_Q(\vec{E},\vec{R}) = \Sigma(L,M) \; Y^*_{LM}(\hat{E}) Y_{LM}(\hat{R})$$

$$*i^L \exp(i\delta_L) \, X^+_L(E,R)/R \tag{2.48}$$

substitution into (2.36), using (2.40) and (2.46), premultiplication by $(2M/\hbar^2) Y_{L'N'}(\hat{E}) Y_{L'N'}(\hat{B})^*$ and integrating over $d\hat{E}$ and $d\hat{R}$ gives

$$\{d^2/dR^2 + (2M/\hbar^2)(E-V_d(R)-L(L+1)/R^2)\} i^L$$

$$*\exp(i\delta_L) \, X_L(E,R) =$$

$$(2M/\hbar^2) \int d\hat{E} \int d\hat{R} \; Y_{LN}(\hat{E}) Y_{LN}(\hat{R})^* \int d\vec{R}' \int d\vec{\epsilon} \; V_{d\vec{\epsilon}}(R)$$

$$*\{ I + II \} V_{\vec{\epsilon}d}(R') \; \Sigma(L',N') \; Y_{L'N'}(\hat{E}) Y_{L'N'}(\hat{R})^*$$

$$*i^{L'} \exp(i\delta_{L'}) \, X_{L'}(E,R')/R' \tag{2.49}$$

where the quantities I and II are given by (2.40) and (2.46), respectively. Asymptotically,

$$\lim_{R \to \infty} X_L(E,R) = A(k)\sin(kR - l\pi/2 + \delta_L) \tag{2.50}$$

where δ_L is the complex partial wave phase shift.

Alternatively for

$$\delta_L = \delta_L^1 + i\delta_L^2 \qquad (2.51)$$

$$X_L = X_L^1 + iX_L^2 \qquad (2.52)$$

we may write

$$X_L^1 = A(k)\cosh\delta_L^2 \, \sin(kR - L\pi/2 + \delta_L^1) \qquad (2.53)$$

$$X_L^2 = A(k)\sinh\delta_L^2 \, \cos(kR - L\pi/2 + \delta_L^1) \; . \qquad (2.54)$$

The phase shift is complex because the potential is complex, the imaginary part of which gives rise to flux loss through ionization.

To further simplify the derivation we need to examine the form of the coupling matrix element $V_{d\vec{\epsilon}}$ of (2.30). We assume that the continuum orbital $\phi(\vec{\epsilon};N)$ in the continuum wavefunction $\phi(\vec{\epsilon};1,2,\ldots N)$ can be expanded in angular momentum partial waves (in the body-fixed frame) as

$$\phi(\vec{\epsilon};N) = \phi(\vec{\epsilon},\underset{N}{r})$$

$$= \sum (l,m) \, Y_{lm}^{*}(\hat{\epsilon}) \phi(\epsilon lm;\underset{N}{r}) \qquad (2.55)$$

and we need to determine how many partial waves l should be retained in the expansion. To the extent that rotational Born-Oppenheimer couplings can be neglected, the most straightforward approach is to proceed as in

Hickman et al. (1977) and Miller et al. (1972) and simply
compute partial widths at various internuclear separations
and determine the minimal number of partial waves l which
have appreciable contribution. If the symmetries of the
resonance and molecular ion states are known, the
projection m of the emitted electron electronic orbital
angular momentum on the internuclear axis can be fixed by
conservation of total electronic orbital angular momentum
projection. That is,

$$m = M* - M+$$

where $M*$ ($M+$) is the projection for the resonance
(molecular ion) state. The tacit assumption here is that
the axial component of the electronic orbital angular
momentum is a good quantum number. In the same spirit
Micha and Nakamura (1975) analyzed molecular orbital
correlation diagrams in the separated- and united-atom
limits for the initial and ion states to deduce a minimal
number of partial waves l which should be included (e.g.,
for HeAr*, HeAr+ this set was l=0,1,2 with l=0 the
dominant contribution). This work was extended (Bellum,
1976; Bellum and Micha, 1977) to include effects of
Born-Oppenheimer rotational couplings to deduce
contributing partial waves for several atom-atom and
atom-ion pairs. Since heavy particle angular momentum is
large (typically cn the order of 10 to 100) compared with
electron angular momentum, we are justified in neglecting

electronic angular momentum in both the initial and final
channels. As it is the object of the present work to
focus on a detailed description of the heavy particle
dynamics in ionizing collisions, we can with justification
simplify our task by considering only the first (l=0) term
in the expansion.

Our previous result (2.49) becomes

$$\{d^2/dR^2 + (2M/\hbar^2)(E - V_d(R)) - L(L+1)/R^2\} X_L(E,R) =$$

$$(2M/\hbar^2) \int dR' \int d\epsilon \, V_{\epsilon d}(R) [\int dE' \, \psi_L(E',R)$$

$$* \psi_L^*(E,R') \{E^+ - \epsilon - E'\}^{-1}$$

$$+ \Sigma(n) \, \psi_L^n(E_L,R) \psi_L^n{}^*(E_L,R')$$

$$* \{E^+ - \epsilon - E_L^n\}^{-1} V_{d\epsilon}(R') X_L(E,R')$$

$$\tag{2.56}$$

and where the right-hand side becomes, on evaluating the
quantity inside [...],

$$R.H.S. = (2M/\hbar^2) \int dR' [\int dE' \, \psi_L(E',R) \{p.v. \int d\epsilon$$

$$V_{d\epsilon}(R) V_{\epsilon d}(R') (E - \epsilon - E')^{-1} - i\pi V_{dE''}(R)$$

$$* V_{E''d}(R') \} \psi_L^*(E',R')$$

$$+ \Sigma(n) \, \psi_L^n(E_L,R) \{p.v. \int d\epsilon \, V_{d\epsilon}(R)$$

$$*V_{\epsilon d}(R')(E-\epsilon-E_L)^{-1} - i\pi \, V_{dE'''}(R)$$

$$*V_{E'''d}(R')\} \, \Psi_L^*(E_L,R') \,] \, X_L(E,R') \tag{2.57}$$

where $E''=E-E'$ and $E'''=E-E_L$ and p.v. denotes a Cauchy

principal-value integral.

The first two terms in [...] in (2.57) are
contributions to the potential from continuum (Penning)
channels and the last two terms are from AI channels. The
result (2.57) clearly demonstrates the non-locality and
energy dependence of the optical potential. Also note
that all discrete and continuum final-channel heavy
particle states of a given L are coupled to the initial
channel motion of the same angular momentum partial wave
L. We symbolically write the last result

$$D_L \, X_L(E,R) = (2M/\not{h}^2)\int dR' \, K_L(E;R,R') X_L(E,R') \tag{2.58}$$

where

$$D_L = [d^2/dR^2 + (2M/\not{h}^2)(E-V_d(R)) - L(L+1)/R^2] \tag{2.59}$$

and the kernel K_L is decomposed as

$$K_L(E;R,R') = K_L^{PI}(E;R,R') + K_L^{AI}(E;R,R') \tag{2.60}$$

or

$$K_L(E;R,R') = \Delta_L(E;R,R') - (i/2) \, \gamma_L(E;R,R') \tag{2.61}$$

and where

$$\Delta_L(E;R,R') = \overset{PI}{\Delta_L}(E;R,R') + \overset{AI}{\Delta_L}(E;R,R') \qquad (2.62)$$

and

$$\gamma_L(E;R,R') = \overset{PI}{\gamma_L}(E;R,R') + \overset{AI}{\gamma_L}(E;R,R') . \qquad (2.63)$$

In contrast to the set of coupled second-order ordinary differential equations we obtained in Section I.3, in the present theory we have a single inhomogeneous differential equation for an "effective" nuclear wavefunction; the complexity of the problem lies in the kernel $K_L(E;R,R')$.

To complete the formalism we need the scattering cross sections for PI and AI. Cross sections for transitions from states i to f are given as the transition rate R_{fi} per unit incident flux; R_{fi} is given by (Micha, 1974)

$$R_{fi} = (2\pi/\hbar)|T_{fi}|^2 \delta(E_f - E_i) \qquad (2.64)$$

where T_{fi} is the relevant transition amplitude. For continuum states normalized to unity on the energy scale

$$\langle \Psi(\vec{E}') | \Psi(\vec{E}) \rangle = \delta(\vec{E}' - \vec{E}) \qquad (2.65)$$

the flux is $k_i^2/[(2\pi)^3\hbar]$.

For Penning ionization the final channel variables are $\vec{E}'$ and ϵ; from the results of Appendix B we have

$$T_{fi}(\vec{E},\vec{E}',\epsilon) = \langle \Psi^-(\vec{E}')V_{ed}X^+(\vec{E})\rangle_Q \quad (2.66)$$

where $\langle...\rangle$ denotes $\int d\vec{R}$. Expanding Ψ and X in partial waves ((2.39) and (2.48), respectively) we obtain the triply differential cross section

$$d\sigma(\vec{E},\vec{E}',\epsilon)/d\vec{E}'d\epsilon = c\delta(E_i - E_f)|T_{fi}|^2 \quad (2.67)$$

where

$$c = (2\pi/\hbar)[(2\pi)^3\mu/k_i^2] \quad (2.68)$$

and

$$|T_{fi}|^2 = |\Sigma(LM) Y_{LM}(\hat{E}') Y_{LM}(\hat{E}) \exp(i\delta_L)$$

$$*\exp(i\delta_L)\int dR \ \Psi_L^-(E',R) V_{ed} \ X_L^+(E,R)|^2 . \quad (2.69)$$

The energy distribution of emitted electrons is obtained by integrating over heavy particle angles and energies and, by choosing the initial relative momentum to lie along the z-axis in the center of mass system, we obtain

$$d\sigma^{PI}(E,\epsilon)/d\epsilon = c|\Sigma(L) \ [(2L+1)/(4\pi)]^{1/2}$$

$$*\exp(i\delta_L)\exp(i\delta_L)$$

$$*\int dR \ \Psi_L^-(E+\Delta-\epsilon,R) V_{ed} \ X_L^+(E,R)|^2 . \quad (2.70)$$

The Penning ionization cross section is simply

$$\sigma^{PI}(E) = \int(0,\epsilon') \ d\epsilon \ d\sigma^{PI}(E,\epsilon)/d\epsilon \quad (2.71)$$

with ϵ' the maximum value of the electron energy for PI,

determined by energy conservation.

For associative ionization the final channel variables are E_J^n and ϵ and we have the amplitude

$$T_{fi}(\vec{E}, E_J^n, \epsilon) = \langle \psi(E_J^n) V_{\epsilon d} X_Q + (\vec{E}) \rangle .$$

$$(2.72)$$

Making partial wave expansions of the heavy particle functions we arrive at

$$|T_{fi}|^2 = [(2J+1)/4\pi] |\int dR \, \psi_J(E_J^n, R)$$

$$*V_{\epsilon d}(R) X_J^+(E, R) \exp(i\delta_J)|^2$$

and the differential cross section per unit energy is

$$d\sigma_J^{AI}(E, E_J^n, \epsilon)/d\epsilon = c\delta(E_i - E_f)|T_{fi}|^2 .$$

$$(2.73)$$

The cross section for formation of the molecular ion in the vibrational-rotational state (n, J) is obtained by integrating (2.73) over ϵ, which gives

$$\sigma_J^{AI}(E, E_J^n) = c[(2J+1)/4\pi] |\int dR \, \psi_J(E_J^n, R)$$

$$*V_{\epsilon''d}(R) X_J^+(E, R) \exp(i\delta_J)|^2$$

$$(2.74)$$

where in the last result we have made use of the energy-conservation relation

$$E + \Delta = \epsilon'' + E_J^n$$

with Δ the asymptotic energy separation between resonance

and molecular ion potential curves. The AI counterpart to the electron energy distribution for PI is a discrete set of lines for the electron energy spectrum. For a particular vibrational state n we have

$$\sigma^{AI}(E,n) = \Sigma(J)\ \sigma^{AI}(E,E_J^n,\epsilon) \tag{2.75}$$

and the total AI cross section (for formation of all possible molecular ion vibrational and rotational states) is

$$\sigma^{AI}(E) = \Sigma(nJ)\ \sigma^{AI}(E,E_J^n,\epsilon) \tag{2.76}$$

This completes our theoretical development of an effective Hamiltonian formalism for ionizing atomic collisions. In the next chapter we will discuss some computational aspects of the coupled channels theory of Section I.3 and present detailed numerical studies of PI of Ar by He(1s2s,^{3}S). In the final chapter we will return to the effective Hamiltonian theory where we present a method of solution for the inhomogeneous second-order ordinary differential equation (2.58).

III.1 Solution of the Matrix Schrodinger Equation

In order to obtain numerical solutions to a set of N
coupled second-order ordinary differential equations
(ODE's) such as (1.18) we must first specify 2N constants.
Regularity of solutions at the origin (1.25) serves to
determine N of these constants, and the remaining N can be
chosen as the values of the first derivatives at the
origin. The specification of the N-dimensional derivative
matrix is otherwise arbitrary so long as it leads to
linearly independent solutions. Suitable choices are the
unit matrix, a diagonal matrix whose elements have "small"
values (such that solutions start out with small slopes)
or, more generally, any non-singular matrix.

Choosing the origin as a starting point is frequently
a source of difficulty, however. Regions interior to
classical turning points of interatomic potentials are
non-classical regions, and it is in these regions that the
solutions decay exponentially with decreasing R. As a
consequence, in outward integration from the origin one is
often plagued by an exponential growth of some of the
solution components and an attendant loss of linear

independence of the vectors. Two remedies suggest themselves: modify the boundary conditions at the origin or periodically orthogonalize the solution matrix. The first choice could be effected by re-specifying the origin at some value of R intermediate between the origin and the classical turning point; the choice of new origin could be by trial-and-error (Bernstein, 1960) or, following Bellum and Micha (1978), by using semiclassical approximations to the wavefunction and derivative and selecting as the origin that value of R at which the slope is less than some specified (usually small) tolerance. In a multichannel problem one may encounter a situation in which the classical turning points are widely separated, so that the origins for each channel will likewise be separated. During the early stages of outward propagation, however, the exponential growth problem may still be present unless one suppresses those solutions with the outermost origins. The presence of centrifugal barriers (also nonclassical regions) in any channel may again tend to introduce linear dependencies requiring periodic orthogonalization of the solutions in these areas.

For the Penning ionization problem, a computer program DEVOG was written to solve a set of coupled second-order ODE's. The algorithm of deVogelaere (1955), generalized by Lester (1968, 1971) to the multichannel

(matrix) case, was selected as the integrator. This is a fourth-order method as is comparable in accuracy to fourth-order Runge-Kutta (RK) methods. As an error-controlled mesh selector (where step-length is modified to satisfy a local error criterion) was not developed for the deVogelaere method until the recent work of Coleman and Mohamed (1979), a fixed step-length algorithm was used. Step size was chosen to be dependent upon the collision energy; typically 10 steps per deBroglie half-wavelength were found to be adequate. A single channel (elastic scattering) option of the program was satisfactorily tested against scattering phase shift results of Bernstein (1960) who employed a standard Runge-Kutta-Gill (RKG) integrator; the coupled channels option was successfully tested against partial wave S matrix elements of Olson and Smith (1971; 1972), where a Numerov integration scheme was used.

For application to Penning collisions we have made a study of the ionization of Ar by He*(1s2s,^{3}S) at thermal energies. A two-state approximation has been invoked: the He* and Ar are assumed to move in a $^3\Sigma$ potential, and the motion of the heavy particles He and Ar$^+$ is governed by a $^2\Sigma$ potential; these are the potentials V_d and V_+, respectively, appearing in (1.34). The functional forms of these potentials, as well as the coupling matrix

elements V_{dJ} (1.34) were those used in previous work (Relyea and Micha, 1979; Bellum and Micha, 1978)) and are given in Appendix A. It should be pointed out that while "realistic" functional forms are chosen for the potentials, the origins of the parameters lie both in theory and experiment and so to this extent serve as models with which we will do detailed dynamical studies. In this connection, the reader is directed to the recent work of Siska (1979a) and Olson and Liu (1978) for a discussion of $^3\Sigma$ and $^2\Sigma$ potentials, respectively. At a collision energy of 65 meV (0.0024 Hartrees) we have computed the PEED (1.31) within the decoupling approximation (1.33) of Chapter I. The step size was chosen to be 1/20-th of the smallest deBroglie wavelength in each of the coupled channels. The discretization basis step size was $\Delta\epsilon = 2.0(10^{-4})$ a.u. for $\epsilon < 0.1503888$ a.u., and $\Delta\epsilon = 0.5(10^{-4})$ a.u. for ϵ greater than this value. In Figure 3 the results are presented for a maximum L value of 50 and a discretization basis of 35 functions. The maximum L value was selected on the basis of convergence of the Penning ionization cross section upon inclusion of higher partial waves. The continuum mesh was decreased for the upper range of electron kinetic energy to more clearly elucidate the structure suggested in the PEED in earlier work (Bellum and Micha, 1978). In

all cases the symmetry of the K matrix (1.26) was better than 1 part in 10^3. Total computation time to solve the coupled equations (1.33) and calculate cross sections was 54 minutes on an IBM 370/165 computer; this is roughly 2 seconds per partial wave and per ϵ, and was faster than the computations of the earlier work by a factor of one-third.

The qualitative features (e.g., overall shape and position of the maximum) are in general agreement with the experimental results of Hotop (1974). That there is more structure in the computed results is not surprising; the widths of the peaks in the computed spectrum are on the order of 10^{-5} a.u. (< 1 meV), whereas experimental spectra, limited by thermally broadened beams and finite detector resolution, have a full-width-half-maximum resolution of 10 - 20 meV (Hotop and Niehaus, 1969). One is led to question whether any interpretation can be given to the structure of the calculated distribution or if the maxima are merely computational artifacts.

As we saw in the last section, the final channel energy E_f is related to the collision energy E, electron kinetic energy ϵ and asymptotic potential energy separation Δ by

$$E + \Delta = \epsilon + E_f \quad ; \qquad (3.1)$$

here E and ϵ are measured relative to the separated-atom

energies of the colliding species in the entrance channel, and Δ and E_f are measured relative to the final channel molecular ion asymptote. The interpretation of the single feature in the PEED of Bellum and Micha (1978) was based upon the notion of an orbiting resonance in the final channel; the colliding particles may become temporarily bound by a centrifugal barrier, increasing the likelihood of reaction during this prolonged encounter. The final channel energy was speculated to lie just above a maximum in the centrifugal barrier for L = 24, the partial wave which dominated the cross section at that peak. In addition, the classical turning point in the initial channel was found to lie directly above this barrier. The combination of these two effects, the increased probability of a transition in the vicinity of a classical turning point and the possibility of some sort of resonant state in the final channel, was thought to explain the enhancement in the spectrum at that particular electron energy.

We have pursued this line of questioning by studying partial wave contributions to the PEED at each value of the emitted electron kinetic energy where there is cross section enhancement; these are labelled (a) - (g) in Figure 3. One first observation was that the classical turning point for the dominant partial wave in the

entrance channel was located above (but not necessarily at the maximum of) a centrifugal barrier for that same L-value in the final channel, consistent with the observation in the earlier work. To facilitate further discussion, Table 1 contains dominant L-value contributions to the PEED, as well as final channel energies and partial wave barrier maxima. For all structures except (e)--the largest one--the final channel energies lie just above the barrier maxima; these may correspond to scattering resonances, where the heavy particles in the final channel have just barely enough energy of relative motion to avoid binding. These states may be loosely thought of as "bound states in the continuum" of nuclear motion, and this opens an interesting area for further study utilizing techniques of molecular electronic structure theory.

The so-called "stabilization" method of Hazi and Taylor (1970) is based upon the observation that in basis-set electronic structure calculations one obtains, from an N-dimensional matrix eigenvalue problem, perhaps M bound (negative energy) states and N-M positive energy states. By adjusting the basis the bound levels will remain stationary (assuming the basis is "good enough" to begin with) while the energy of the scattering states fluctuates; in the event that there are "virtual" levels whose energies do not change with basis set adjustment,

these levels are said to have been "stabilized" and are termed resonances, bound states in the continuum or autoionizing electronic states. Turning to the nuclear motion problem, the same basis set techniques can be applied to determine the vibrational-rotational states of molecules (Shore, 1973; 1975; Davis and Heller, 1979). For very high, diffuse (but bound) levels, basis sets tend to be quite large and there is parameter adjustment which must be done, since one wishes to describe both very spatially localized, low-lying levels as well as these highest states in the same basis; usually an improvement in the description of the highest levels comes at the expense of the lower eigenvalues. For scattering states a still larger basis set would be required. There would also be a "termination" error associated with the fact that the scattering states do not obey boundary conditions appropriate to bound states; we must put our particles in a "box" to do the basis set calculation. In this connection one could employ a scattering-like basis (e.g., oscillatory functions) and now the termination error would apply to the bound levels rather than the positive energy states. The problems discussed here are technical rather than theoretical, however, and it remains to be demonstrated whether one can implement this methodology to obtain "bound states in the continuum" of nuclear motion.

Returning to our discussion of the structure in the electron energy spectrum, the explanation of peak (e) is readily obtained with the use of Figure 4. Here we depict the initial and final state effective potentials for the dominant partial wave (L = 24) and note that the final channel energy lies <u>below</u> the barrier maximum; this is a predissociating state, and one could in principle obtain its width and lifetime. States of this kind have long been observed in diatomic molecule absorption spectra; unlike sharp bound-bound lines, the decay of the predissociating state results in a broadened spectral line, reflecting the finite lifetime of the excited species. It is not surprising that there is a marked enhancement in the PEED under these conditions; the longer the particles remain bound, the greater the likelihood of electron emission. Before leaving the discussion of electron spectra it is difficult to resist the following speculation: rather than "fold" our computed results with (unknown) distribution functions (to account for ncn-monoenergetic atomic beams) and "acceptance" functions (to account for detector resolution), it is instead hoped that as the experimental work in this area becomes more refined, observation of quantum effects such as those discussed in this section will be able to provide a more stringent test of the theory.

At this point we would like to elaborate on a

possible reaction "mechanism" for Penning ionization. A study of molecular orbital correlation diagrams (Bellum and Micha, 1977) pictured the ionization as a molecular Auger-type process, going through a quasimolecular intermediate from which an electron is ejected. In the specific case of He*(1s2s, ^{3}S) + Ar, a simple interpretation has a "hole" in He* going over into a hole in the quasimolecule; an electron from a higher σ molecular orbital (with predominantly Ar 3p character) "falls" into the hole and the outermost orbital (singly occupied and strongly He* 2s in character) is ionized resulting in a $^2\Sigma$ molecular ion.

Alternatively, we might ask whether electron emission actually occurs from the quasimolecule AB*, or from another state more closely resembling (AB$^+$,e$^-$). This question arises from the fact that we have rationalized the PEED structures in terms of quasimolecular states in the final, molecular ion channel, not in the initial channel; electron emission is favored when HeAr$^+$ is temporarily trapped in a centrifugal barrier. Initial channel resonances could certainly be used to explain enhancements to the cross section from certain partial waves as the colliding particles would be held by a centrifugal barrier long enough for electron emission (or exchange plus emission) to occur. To test this hypothesis we have examined the initial channel for centrifugal

barriers and have found that 1) for L > 18 the effective potentials are purely repulsive, and 2) for L < 18 the largest barrier height was twenty times _less_ than the collision energy (65 meV) and that these maxima occurred at internuclear separations greater than about 11 bohr. Thus there is little likelihood of initial channel resonances of this type affecting the cross section as in Figure 3.   Initial channel resonance behavior would be more likely to contribute to PEED structure and larger PI cross sections at much lower collision energies (in light of remark 2) above) and it would be interesting to extend the work presented here to much lower energies to test this hypothesis. A rise in the ionization cross section at lower energies would be consistent with the semiempirical work of Olson (1972) and which has already been seen in PI of Kr by Ne* (Weynaber and Magnuson, 1976) and of Ar by Ne*(Micha et al., 1971; Tang et al., 1972).

Consequently we are left with the notion of final channel resonances as an explanation for our PEED results and we conclude from this that a HeAr+ -like state must be formed _prior_ to electron ejection; the system may evolve as

$$He* + Ar \longrightarrow HeAr* \quad (quasi\text{-}molecule\ formation)$$

$$HeAr* \longrightarrow (HeAr^+ ,\ e^-) \quad (Auger\ process)$$

$$(HeAr^+ ,\ e^-) \longrightarrow HeAr^+ + e^- \quad (electron\ emission)$$

$$HeAr^+ + e^- \longrightarrow He + Ar^+ + e^- \quad (break\text{-}up)$$

with final channel resonance contributions in the third step. The final channel maximum occurs away from the potential minimum and we may think of HeAr⁺ in this state as already approaching its asymptotic limit of He + Ar⁺. Although Rydberg-like states were not included in our electronic expansion basis which gave rise to the coupled channels equations it seems possible that the transition may proceed through a state in which an electron is loosely bound to a HeAr⁺ ground state core. We then see a dramatic effect of nuclear motion upon ionization probability: our initial state undergoes an Auger-type transition to an intermediate resembling an electron loosely bound to HeAr⁺, and through continued interaction--facilitated by rotational trapping--the likelihood of ionization is increased.

At this point it is desirable to examine--by way of numerical studies--the validity of the decoupling approximation of Chapter I; e.g., how do the the results of the 35 (decoupled) 2-state calculations compare with those of the exact matrix problem of dimension 36 ? The motivation for this study was made clear in the first chapter; recall that with the neglect of the continuum-continuum couplings, the potential matrix U blocked in such a way as to make decoupling a physically appealing approximation. There are several considerations which mandate caution in proceeding to solve the

higher-order matrix differential equation. One factor is the linear dependence problem already discussed; there is a strong likelihood that non-classical regions will impede efficient numerical solution. We could suppress certain solutions as has been already suggested, but in the event of propagation through centrifugal barriers this is not justified. A more practical problem is the anticipated expense of such a study. Results of Allison (1970) suggest that for the deVogelaere algorithm the time goes as approximately $N^{2.5}$ where N is the number of coupled equations (here, the number of discretization basis functions plus one). With this figure our anticipated CPU time, per collision energy, is roughly 40 hours; this study, much less a PI energy-dependence study, is clearly impractical using this technique. Lester (1971) indicates that the deVogelaere algorithm is to be preferred to Numerov and RK methods based upon consideration of stability, storage requirements and machine time. Although the piecewise-analytic approach of Gordon (1971) was not included in the analysis, that method is claimed to have an N^3 dependence; unlike numerical methods, the step size is not related directly to the collision energy (or deBroglie wavelength) so that fewer steps may be required. It seems unlikely, however, that there will be adequate savings to make even this method desirable for our applications. In the following section we discuss the

implementation of a rather recently-developed method for the solution of a set of coupled <u>first</u> order ODE's which will have practical consequences for our study of Penning ionization.

III.2 Solution of a Matrix Riccati Equation

In the preceding section we demonstrated the need for a new computational approach if we wished to assess the validity of the decoupling approximation of Chapter I. As it is only asymptotic information (e.g., K matrix) which is of importance to us, any equivalent formulation of the problem capable of giving us the desired information is acceptable. One such approach is given here. Transform the matrix Schrödinger equation for the wavefunction (suppressing partial wave indices)

$$D \ X = U \ X \tag{3.1}$$

by use of

$$y = X' \ X^{-1} \tag{3.2}$$

(where prime denoted differentiation with respect to R) into a matrix equation for the logarithmic derivative

$$y' + W + y^2 = 0 \tag{3.3}$$

where

$$W = (2M/\hbar^2) \{E1 - V - Z\}. \tag{3.4}$$

Here **V** is the effective potential matrix (including centrifugal potenial), **Z** a diagonal matrix of channel

threshhold energies and **1** the unit matrix. The boundary condition on X at the origin gives for $y(0)$ a diagonal matrix with infinite elements; owing to the symmetry of V, $y(R > 0)$ is symmetric. Usual numerical techniques for solving (3.3) cannot be applied because y diverges for certain values of the argument (whenever X has a node). A derivation of an algorithm for the solution of (3.3) which circumvents this problem and which is based upon a limiting form of the "amplitude-density" equations of Johnson and Secrest (1966; 1968) may be found in Appendix B. The first published application of the method to scattering problems (Johnson, 1973) demonstrated its advantages over methods for solving the second order matrix differential equation in regard to selection of starting points, propagation through classically forbidden regions and computation time. A more recent extension of the method has been to the bound-state solutions of the one-dimensional Schrödinger equation (Johnson, 1977), an extreme test of stability in propagation through non-clasical regions.

Returning to the asymptotic form of X (1.26) we can write for K :

$$K = -\{yN-N'\}^{-1}\{yJ-J'\} \qquad (3.5)$$

where N and J are given by (1.27,1.28) and (1.35,1.36) for open and closed channels, respectively. Symmetry of y results in symmetry of K, and K may be again partitioned

into submatrices (1.37). In the following section we report on implementation of this method for a study of the Penning ionization of Ar by He*(1s2s,^{3}S) at thermal energies.

III.3 Application to PI of Ar by He*(1s2s,^{3}S) at Thermal Energies

A program LOGDERIV was written to solve the Riccati transform (3.3) of the matrix Schrödinger equation for Penning ionization in atomic systems. Before discussing applications to physical problems, it is appropriate to relate certain observations on the numerical method. As already mentioned, $y(0)$ is a diagonal matrix with infinite matrix elements. Johnson (1973) suggests replacing this by

$$y(0) = c\mathbf{1} \qquad\qquad (3.6)$$

where c is a large number (e.g., 10^{20}). We examined the asymptotic solution y for a number of choices of c ranging from 10^{40} to 10^{-20} and in all cases the solutions were identical to 15 decimal digits; hence, the choice of $y(0)$ is quite arbitrary, and this is a reflection of the fact that for the second-order ODE there was considerable flexibility in specification of the first derivatives. The location of the origin was varied inside the classical turning point and the finding was the same, and we conclude (as did Johnson (1973)) that the algorithm is highly insensitive to starting conditions. Another point

we note is that, from the results of Appendix C, the
algorithm requires a matrix inversion at every integration
step. This suggests that the matrix inversion will be the
time consuming operation in the propagation. For the
matrix inverter we used a routine due to Beebe (1978)
which is based upon the successive orthonormalization
procedure of Löwdin (1968) and which we verified through
numerical studies to be an N^3 method. Timings were made
on LCGDERIV using this routine and, based upon studies of
up to 50 coupled equations, a very clear N^3 dependence was
evidenced here as well.

Returning to the present application, the code was
tested against various scattering problems in the
literature, and in all cases the results were
satisfactory. For elastic scattering we again compared
with the phase shift results of Bernstein (1960); for
multichannel problems with only open channels we compared
with R (or K) matrix elements from an exactly soluble
two-state model (Harris and Michels, 1969) and with
transition probabilities for He+ + Ne inelastic
scattering (Johnson, 1973) using potentials and couplings
of Olson and Smith (1971). The inclusion of closed
channel boundary conditions was compared with partial wave
cross sections of Matese and Henry (1972) for a model
problem which has some of the features of low-energy
electron-hydrogen scattering.

For PI we first studied the convergence of the transition probability as a function of discretization basis size for the "exact" matrix problem (1.18). The basis was that of Section I.3 and we spanned a fixed interval of the electronic continuum with an increasing number of basis functions. In Figure 5 we present a typical convergence study for PI of Ar by He*(1s2s, ^{3}S) at a collision energy of 65 meV; the results for L = 0 demonstrate that convergence is obtained with twenty or so basis functions, and similar behavior was noted for other partial waves and at other energies. Thus, for all further results to be reported in this section, the benchmark was a matrix problem of dimension 20, and this will be compared with the decoupling results of 19 two-state calculations.

We wish to examine the validity of decoupling as a function of two dynamical variables in the theory, namely the heavy particle angular momentum partial wave L and the collision energy E. In Figure 6 the L = 0 partial wave contribution to the PEED is shown for a collision energy of 65 meV and it is seen that the agreement between exact and decoupled results is quite good. At the same energy results are shown for L = 24 in Figure 7, and in Figure 8 are L = 0 results at 125 meV. Our general conclusion from these and other results is that the decoupling approximation is highly satisfactory and that its accuracy

exhibits no dependence on collision energy (at least over the range of interest) or on heavy particle angular momentum partial wave. The results in Figures 6-8 are not the whole story, however, as one must, at each collision energy, sum over L to obtain a PEED (1.31) and integrate over ϵ to give the Penning ionization cross section. In Figure 9 we show a PEED at 65 meV and discover, in keeping with the partial wave findings, good agreement between exact and decoupled results. Although the continuum mesh was larger here than in the study in Section III.1, the structure in Figure 9 again arises from a dominant partial wave (L = 24). That such structure was evident when using an entirely different computational approach lends support to the interpretation given such peaks in Section III.1; they are decidedly not artifacts of the calculation. It is highly instructive to point out that the computations of Figure 9 required about 124 minutes CPU for the 20-state case and about 8.7 minutes for the decoupled calculations on an Amdahl 470/V6 computer; this is roughly 8 seconds versus 0.5 seconds per partial wave and per ϵ. This clearly indicates that "benchmark" calculations are obtainable at a not excessive cost and that a cross section energy-dependence study is a feasible project to undertake.

In this regard, our last effort in the present coupled channels work on PI is to study the Penning

ionization cross section over a range of collision
energies in the thermal energy range (here from 26 - 95
meV) where a variety of experimental work is available
(Illenberger and Niehaus, 1975; Pesnelle et al., 1975;
Wang et al., 1976; Woodard et al., 1978); our results are
presented in Figure 10. We see that at higher energies the
rise in the experimental result begins to decrease. This
may be understood on rather general grounds by considering
such factors as the duration of collision, the distance of
closest approach of the particles, and the strength of a
coupling potential. At low energies the particles may
spend appreciable time in an "interaction region" but at
such a distance that the coupling (or transition) strength
is quite small. As energy increases, the particles
interact for a shorter period of time but the increased
coupling strength at shorter distance drives the reaction.
At still higher energies (not displayed on this figure)
the particles approach closer together and the coupling is
stronger, but the decreased collision time is the dominant
factor and the cross section decreases.

While the agreement between theory and experiment is
good at low energies it clearly deteriorates at the higher
energy end. There are several factors which could
influence this behavior: 1) the coupling potential
(Bellum and Micha, 1978) was parametrized based upon
consideration of autoionization widths at 65 meV, so that

as one gets too far away from this energy (higher or lower) it is not likely to be a realistic coupling. 2) We have neglected to include associative ionization channels in our coupled channels theory; the effect of this process can be seen in the experimental results of Pesnelle et al. (1975): the AI cross section is small at low energies (20 meV), rises to a maximum at about 100 meV and falls off again. To the extent that PI and AI are competing processes it may be reasoned that the inclusion of AI in the theory might tend to bring the entire curve down somewhat, with the shift being greatest at the high energy end of Figure 10. 3) The reliability of the potentials themselves may be questioned. This aspect of the problem has been discussed earlier and we reiterate here that our emphasis has been on a detailed study of the dynamics of the heavy particles in collisional ionization, with more-or-less reasonable interatomic potentials and couplings. It is not intended that the potentials employed here should be capable of reproducing a wide variety of experimental results; in fact, in semiclassical and optical-model studies it is evident that high and low energy data cannot be reproduced by one set of potential parameters (e.g. Woodard (1978)). Where there has been an attempt to "invert" differential elastic scattering cross section data to obtain the relevant potentials, there is considerable discrepancy between the resulting curves

(Brutschy et al., 1976; Wang et al., 1976; Altpeter et al., 1977; Siska, 1979b). It is hoped that the discussion in Section II.1 of electronic states appropriate to chemi-ionization processes will serve to guide theoretical efforts in this regard.

Figure 2 Potential Energy Curves for PI and AI of Ar by He*(1s2s,^{3}S); note the change of scale on the ordinate for the lower curve.

POTENTIALS FOR PI AND AI OF AR BY HE*(1s2s,3S)

U (A.U.) [X10^-2]

R (BOHR)

He*(1s2s,3S) + Ar (1Σ)

He + Ar+ (2P) (2Σ)
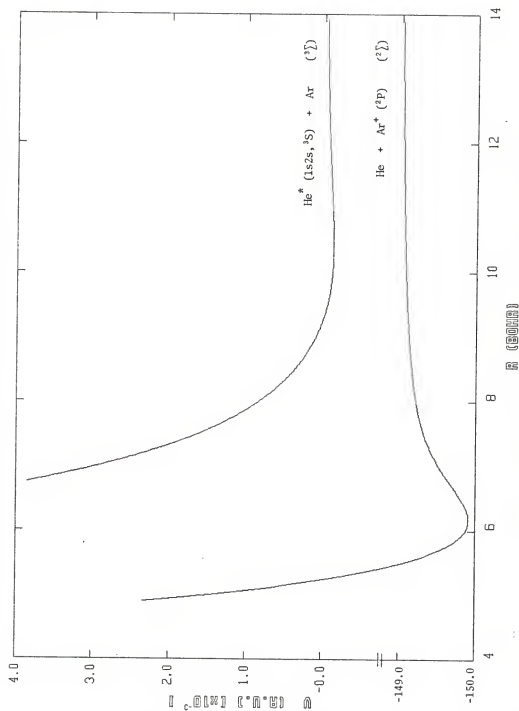
INEN: McIntosh Plot System - Mexico   16/03/80   23.10.59

Figure 3   Penning Electron Energy Distribution
(PEED) for PI of Ar by He* at 65 meV;
results obtained with DEVOG. The
abscissa has been shifted by the asymptotic
energy separation of the metastable and
molecular ion potential curves, 0.149 a.u.

He*(1s2s,2S) + Ar , E=85 meV

ELECTRON KINETIC ENERGY (A.U.) [×10⁻³]

P E E B (SQ.ABMR/A.U.) [×10⁻³]
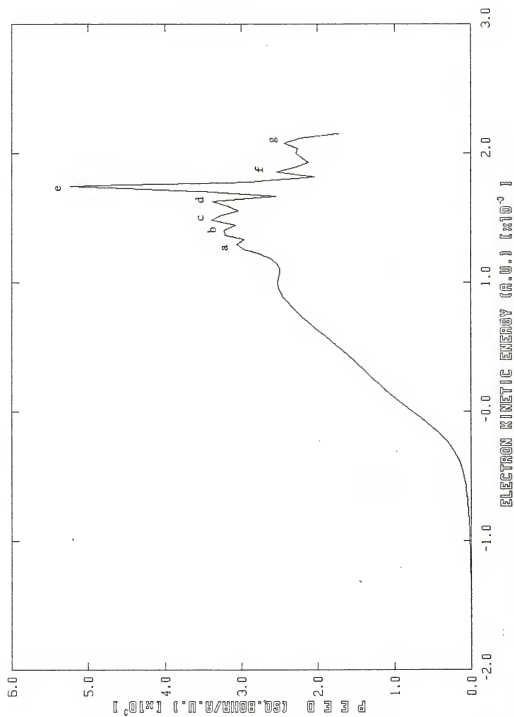
INEN, McIntosh Plot System - Mexico   15/04/80   01.20.54

Table 1

Partial Wave Contributions to PEED of Figure 3

peak	ϵ(a.u.)	E_f (a.u.)	L	% Contrib.	v_{max}^L (a.u.)
a	0.1504388	9.5 (−4)	29	25	9.219 (−4)
b	0.1505388	8.5 (−4)	28	27	8.882 (−4)
c	0.1506388	7.5 (−4)	27	27	7.495 (−4)
d	0.1507888	6.0 (−4)	25	24	5.967 (−4)
e	0.1508888	5.0 (−4)	24	56	5.273 (−4)
f	0.1509888	4.0 (−4)	20	13	2.943 (−4)
			19	18	2.472 (−4)
			18	16	2.046 (−4)
g	0.1512388	1.5 (−4)	16	27	1.336 (−4)

Figure 4   L = 24 Effective Potentials for HeAr* and HeAr+. Dashed lines indicate relative kinetic energy of heavy particles in initial and final channels. Vertical line denotes a Franck-Condon-like transition. The lower curve has been shifted upward by 0.148 a.u. for clarity.

He$^+$ (1s2s,3S) + Ar , E = 65 meV

Effective Potentials (L = 24) [x10^{-3}]

R (Bohr)

E_i

E_f

INEN, McIntosh Plot System - Mexico   18/04/80   15.27.14
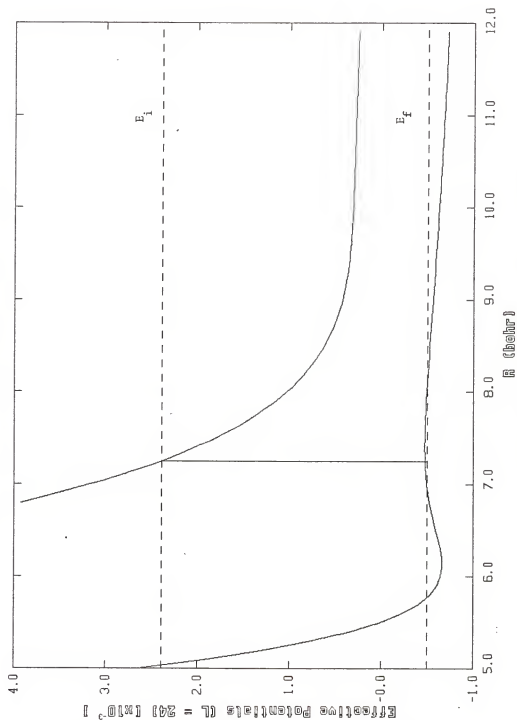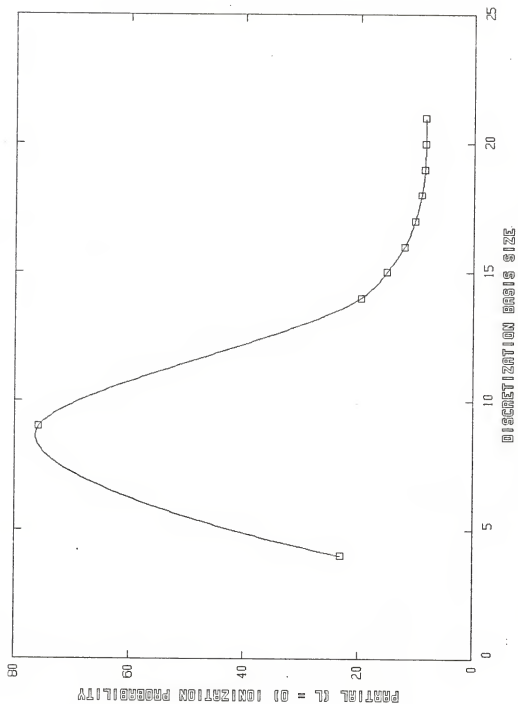
Figure 5   Basis Set Study of L = 0 Partial Wave
           Probability of P1 of Ar by He* at 65 meV;
           results obtained with LCGDERIV.

HE* ✧ RR ⬠ B5 meV

PARTIAL (L = 0) IONIZATION PROBABILITY

DISCRETIZATION BASIS SIZE

IMEN. McIntosh Plot System - Mexico 16/03/80 23.11.02

Figure 6   L = 0 Partial Wave PEED for PI of Ar by He*
at 65 meV. The solid curve corresponds to the
exact matrix calculation of dimension 20,
the broken line to 19 2-state calculations.
The abscissa has been shifted by the asymptotic
energy separation of the metastable and
molecular ion potential curves, 0.149 a.u.

HE* + AR . 85 meV

ELECTRON KINETIC ENERGY (A.U.) [x10⁻³]

INEN: McIntosh Plot System - Mexico   08/04/80   12.23.43
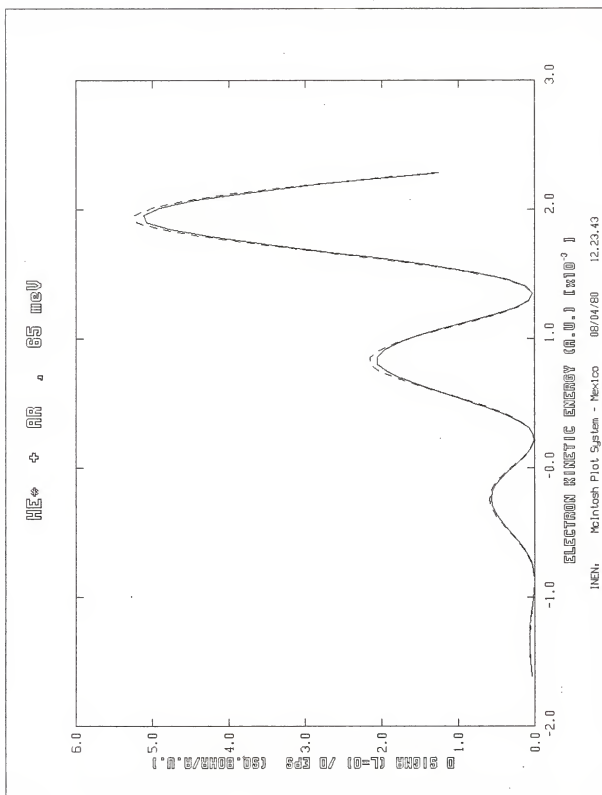
Figure 7 L = 24 Partial Wave PEED for PI of Ar by
         He* at 65 mev. Details of the plot are
         otherwise as in Figure 4.

HE* + AR , 85 meV

D SIGMA (L=54) /0 EPS (SQ.BOHR/A.U.) [x10⁶]

ELECTRON KINETIC ENERGY (A.U.) [x10⁻²]
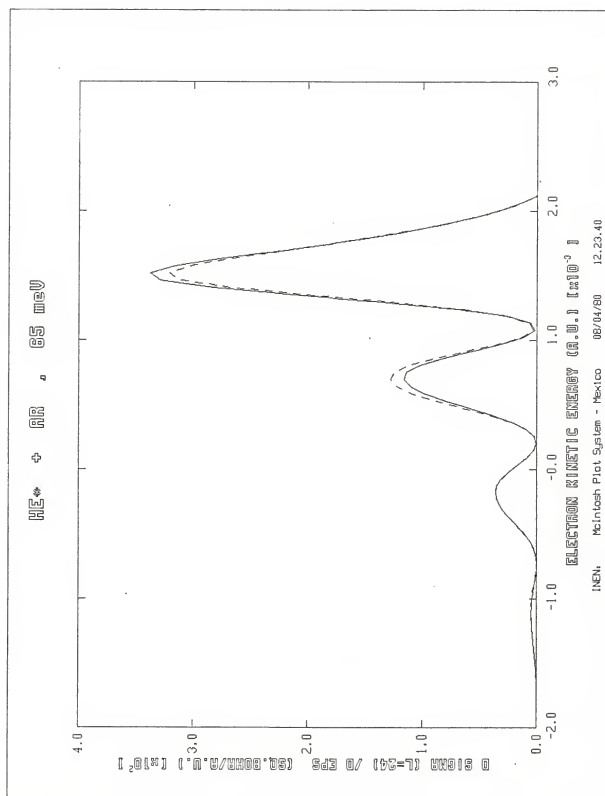
INEN. McIntosh Plot System - Mexico   08/04/80   12.23.40

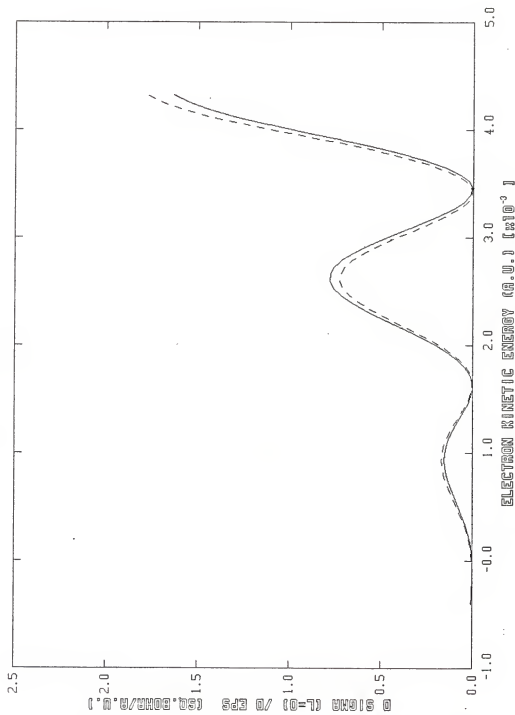Figure 8 L = 0 Partial Wave PED for PI of Ar by He* at 125 mev. Details of the plot are otherwise as in Figure 4.

HE* + AR . 125 meV

ELECTRON KINETIC ENERGY (A.U.) [x10⁻³]

INEN: McIntosh Plot System - Mexico   08/04/80   12.23.41

Figure 9 Total PED for PI of Ar by He* at 65 meV.
Details of the plot are otherwise as in
Figure 4.

HE*(1s2s,3S) + AR , E=85 meV

(20 x 20)

19 (2 x 2)

P E E 0 [50.68MHz/A.U.] [x10²]

ELECTRON KINETIC ENERGY (A.U.) [x10⁻³]
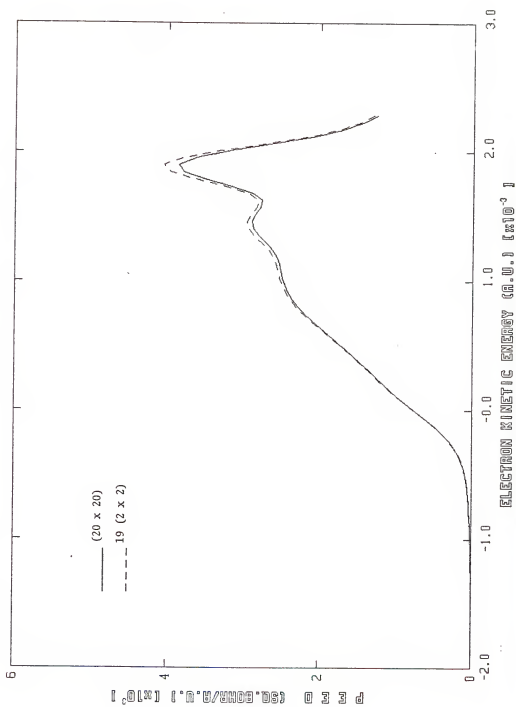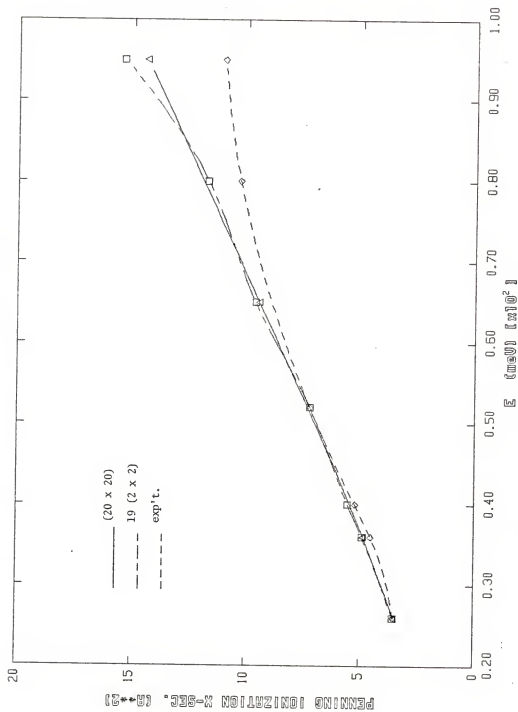
INEN: McIntosh Plot System - Mexico   16/03/80   23.11.03

Figure 10   Cross Section for PI of Ar by He* .
The dashed line is the experimental result
of Illenberger and Niehaus (1975).

HE*(|=2S,3S| + AR

PENNING IONIZATION X-SEC. (A**2)

E (m=V) [x10²]

(20 x 20)
19 (2 x 2)
exp't.

INEN: McIntosh Plot System - Mexico   16/03/80   23.11.02

SOLUTION OF AN INHOMOGENEOUS DIFFERENTIAL EQUATION
FOR PENNING AND ASSOCIATIVE IONIZATION

IV.1 Approximations to a Complex, Non-Local Kernel

We have derived an equation for initial channel heavy particle motion governed by a potential which is complex, non-local and energy dependent. This wavefunction is needed to compute various scattering cross sections of Section III.2. Before specifying a method for solution of the inhomogeneous second-order ordinary differential equation (2.58), we will in this section examine the different contributions to the kernel to see whether simplifications can be made. In the next sub-section we review some traditional approximations to the complex kernel; the validity of these approximations will be investigated in the following sub-section.

IV.2.1 Assumptions Leading to a Local, Imaginary Potential Kernel

Let us first focus our attention on the "electronic" contribution to the kernel from PI and AI; we had in (2.57) the terms

$$p.v. \int d\epsilon \, V_{d\epsilon}(R) \{E-\epsilon-E'\}^{-1} V_{\epsilon d}(E') -$$

$$-i\pi V_{dE''}(R) V_{E''d}(R') +$$

$$p.v. \int d\varepsilon \, V_{d\varepsilon}(R) \{E - \varepsilon - E_L^n\}^{-1} V_{\varepsilon d}(R') -$$

$$-i\pi V_{dE'''}(R) V_{E'''d}(R') \qquad (4.1)$$

with $E''=E-E'$ and $E'''=E-E_L^n$ for PI and AI, respectively.

In the first term E' is a continuous variable corresponding to the allowed final heavy particle states of PI; in the third term E_L^n corresponds to a bound vibrational and rotational level for AI. Two approximations can be introduced at this point to reduce the complex and non-local potential $QHPG+PHQ_P$ to an imaginary one which is local. The first step is to assume (Bieniek, 1978; Nakamura, 1972) that the coupling matrix element $V_{d\varepsilon}(R)$ is essentially independent of ε (the validity of this assumption will be examined more closely in the next sub-section); the terms Δ_L^{PI} and Δ_L^{AI} of (2.62) are zero and we are left with an imaginary, non-local but separable kernel

$$K_L(E;R,R') = -i\pi \, y_L(E;R,R') = -i\pi *$$

$$\{ \int dE' \Psi_L(E',R) V_{dE''}(R) V_{E''d}(R') \Psi_L(E',R')^*$$

$$+ \sum(n)\ \Psi_L(E_L^n,R)V_{dE'''R}^{*}$$

$$V_{E'''d}(R')\Psi_L(E_L^n,R')^{*} \}$$ (4.2)

As a further approximation, we note that the kernel contains products of the form ΨV; the coupling V decays exponentially with increasing R and the functions Ψ oscillate in the potential well region and then either decay (AI) or oscillate (PI) asymptotically. This suggests that ΨV is peaked in ϵ for a value of ϵ around the Franck-Condon value ϵ_v, with the result that V can be

factored out of the sum and integral in (4.2). Using the completeness relation for the set of heavy particle functions allows us to write

$$K_L^{loc}(E;R,R') = -i\pi V_{d\epsilon_v}(R)V_{\epsilon_v d}(R')\delta(R-R')$$ (4.3)

where we choose for ϵ_v, using electronic adiabaticity,

$$\epsilon_v = \epsilon_v(R) = V_d(R) - V_+(R)$$ (4.4)

which is just the vertical energy difference between the resonance and ion electronic energies. With this result equation (2.58) now reads

$$D_L X_L(E,R) = -(2M/\cancel{h}^2)|V_{d\epsilon_v}(R)|^2 X_L(E,R)$$ (4.5)

or

$$\{d^2/dR^2 - (2M/\hbar^2)(V_d(R) - i\gamma(R)/2)$$

$$+ 2ME/\hbar^2\} X_L(E,R) = 0 \qquad (4.6)$$

with

$$\gamma(R) = 2\pi|V_{d\epsilon_v}(R)|^2 \qquad (4.7)$$

Although originally starting from an electronically nonadiabatic description, the result (4.6) has reduced (to within neglect of the real part of the complex level shift) to the result of Nakamura (1969), Fujii et al. (1970) and Miller (1970) where an adiabatic description was assumed from the start.

IV.1.2 Real Part and Non-Local Nature of the Potential Kernel

In light of the approximations just discussed, it is instructive to examine the contribution of the p.v. integrals to the kernel and thus to the real part of the optical potential. Quadrature rules for p.v. integrals have been developed by Elliott and Paget (1979) assuming the functional dependence of the integrand upon the integration variable is known. However, using ab-initio electronic wavefunctions to compute coupling matrix elements and autoionization widths is a fairly difficult task, and the ϵ-dependence of the coupling matrix element is generally not explicit. One approach would be to fit the product of couplings to a function of ϵ for which the

p.v. integrals can be evaluated analytically. In the present work we can obtain an estimate of their contribution in a manner which suffers from none of the above drawbacks. We have already seen (Appendix A) how the coupling matrix element can be given a simple ϵ-dependence based upon a Coulomb representation of the continuum orbital; for this case the p.v. integrals may be done analytically, and the real part of the PI contribution to (4.1) becomes

$$A_L^{PI}(R,R',E,E') = (2/\pi)(2M/k^2)^{-1/2}$$

$$V_{d\epsilon}^{rad}(R)V_{\epsilon d}^{rad}(R') \{ (E'')^{-1/2} \tag{4.8}$$

$$\ln|[(\epsilon'+(E'')^{1/2})/(\epsilon'-(E'')^{1/2}]|-i\pi(E'')^{-1/2}\}$$

where $E''=E-E'$ for PI; a second term $A_L^{AI}(R,R',E,E_L^n)$ is of the same form but where $E''=E-E_L^n$; ϵ' is the maximum possible value of ϵ, determined by energy conservation. $V_{d\epsilon}^{rad}(R)$ is the radial (R-dependent) part of the coupling, given in Appendix A. Evaluating (4.8) and its AI counterpart over a range of E' appropriate to PI and for values of E_L^n corresponding to the L=0 vibrational states of the ion, the real part was found to be of the same

magnitude as the imaginary part. Furthermore, over this range of final channel energies the real part decreased monotonically but the overall change was less than 1%. Whether the ϵ-dependence of our coupling is an accurate one would need to be demonstrated by actually computing couplings using electronic wavefunctions such as those suggested in Chapter II. In this connection, Hickman et al. (1977) observed that for HeH*, a 10% increase (decrease) in k (= $\epsilon^2/2$) causes roughly a 20% decrease (increase) in the autoionization width. For our parametrizaton of the coupling, the same change in k results in about a 10% change in a computed width. Although a strict comparison is of course unrealistic, our results indicate an ϵ-dependence of roughly the same magnitude, and we tentatively conclude that evaluation of p.v. integrals with realistic coupling matrix elements will yield a weak final channel energy dependence similar to that observed here.

Since dependence of the A_L on E' and E_L^n was observed to be weak, the A_L can be taken outside the integral over E' and the sum over n in (4.2). Using the completeness relation for the heavy particle functions for PI and AI and combining terms we obtain, for the contribution of the p.v. terms to the potential, the result

$$V_L^{pv}(R,E,E_v) = A(R,R,E,E_v)$$

(4.9)

where, consistent with the locality approximation, a plausible choice for E_v is that obtained by assuming a Franck-Condon like transition for the nuclei (i.e., one in which the local relative kinetic energy of the nuclei is conserved):

$$E - V_d(R) = E_v(R) - V_+(R) .$$

(4.10)

Before proceeding to discuss the imaginary part of the kernel, we will from this point on assume that, in the general case, the p.v. integrals are obtainable and that a local approximation to the result has been added to the initial channel potential $V_d(R)$. The relative magnitude of V_L^{pv} as compared with V_d has no bearing upon future developments. The key step in the above treatment was the recognition that a local approximation to the p.v. results seems to be quite reasonable. If we were not able to make this local approximation, we would have to carry along a non-local, real contribution to the kernel. Implications of this are discussed in the next section.

Turning our attention to $\mathcal{Y}_L(E;R,R')$, the imaginary part of the kernel composed of PI and AI contributions, the local approximation may also be studied. This is a

much more severe approximation; whereas the real part (local or non-local) of the kernel is essentially a perturbation to V_d, the imaginary part is responsible for decay by electron emission. A local approximation here disallows the possibility of any effect of the relative motion upon the ionization. In light of our interpretation of the PEED structure in Chapter III, there is support for the idea that, at least for PI, electron ejection may have strong dependence upon the relative nuclear motion. We may ask whether the same can be said for AI where the heavy particles remain bound after ionization and the electron energy spectrum is discrete. To help understand the AI process we would like to calculate $\gamma_L^{AI}(E;R,R')$ given from (2.57) by

$$\gamma_L^{AI}(E;R,R') = -i\pi \sum(n) \psi_L(E_L^n,R)$$

$$*V_{dE'''}(R) \psi_L(E_L^n,R') V_{E'''d}(R') \qquad (4.11)$$

with $E''' = E - E_L^n$ and where the sum runs over all vibrational levels of the ion, in our case $HeAr^+$. To this end a program VIBROT was written to determine bound state solutions to the radial Schrödinger equation. Following LeRoy and Bernstein (1968), Cashion (1963) and Cooley

(1961), at a trial energy a solution was integrated inward from some "asymptotic" point until the outermost maximum is located; another solution is propagated outward from an interior point to the point of outermost maximum. Both solutions are scaled to unity at the matching point. A correction to the energy, based upon the difference in slopes at the match point, is calculated and the process is repeated until convergence is achieved; the solution is then normalized. The vibrational quantum number is identified by counting the nodes in the solution. In our application the Numerov method was chosen as the integrator. The program was successfully tested on the bound states of a Morse oscillator, whose eigenvalues are known analytically for L=0.

The 49 bound vibration-rotation levels of HeAr$^+$ are given in Table 2. In this connection we note that 7 quasibound levels were found; these are summarized in Table 3. Quasibound states here are those which are temporarily trapped in a centrifugal barrier but whose energy lies above the threshhold for dissociation. These states have a lifetime t_r and a width (energy uncertainty) γ_r related by

$$t_r = \hbar/\gamma_r . \qquad (4.12)$$

For these resonance levels the outermost boundary

condition was that the wavefunction behave as an Airy function of the second kind (Abramowitz and Stegun, 1972) at the third turning point. This Airy function exponentially increases in extreme non-classical regions, is easy to calculate for small arguments (such as near turning points), and was found to result in more accurate eigenvalues than other choices for outer boundary conditions (LeRoy and Bernstein, 1971). The semiclassical approximation to t$_r$ based upon the vibrational period and barrier tunneling probability given in LeRoy and Bernstein (1971) was used to calculate the results in Table 3. These results are presented here because in addition to "pure" AI there may be long-lived molecular-ion states whose detection depends upon their lifetime and on experimental detection time. At a typical detection time of 10^{-6} seconds (Hickman and Morgner, 1976) only the n=1, L=14 level is likely to be "observed" as dissociated products; most of the quasibound states can thus be treated as true AI. The existence of such states suggests that the sum over bound states appearing in this theory be modified to include quasibound, positive-energy states as well. For these energies the electron energy spectrum corresponding to these levels will overlap with the PEED; there will be discrete lines embedded in the electron energy distribution at the corresponding energies.

In Figures 11 and 12 we plot the vibrational wavefunctions for HeAr$^+$ for L=0, n=0-5. What is surprising is the spatial extent of the levels n=3,4,5; recall that the position of the potential minimum is about 6 bohr. It is of concern to us that the long-range wavefunctions will contribute to the imaginary part of the kernel and thus to the effective potential. However, we see that the kernel is a product of bound wavefunctions with potential coupling matrix elements; the latter have an exponentially decreasing R-dependence and we expect that any contributions from the long-range wavefunctions will be minimized.

Returning to our discussion of the imaginary part of the kernel for AI, we have plotted in Figures 13-18, at a collision energy of 65 meV, the individual terms (to within a factor -iπ) in the sum over n in (4.2); since the kernel is symmetric in R and R' the "hidden" part of the figures can be readily visualized. For n=0 the kernel is everywhere positive since the vibrational wavefunction is nodeless. For n=1-5 only two undulations are observed, and these are at distances in the region of the potential well; the exponentially decaying coupling damps out any oscillatory behavior at large R. In Figure 19 the "sum over states" kernel is shown; it is dominated largely by the n=0,1 vibrational levels since only their wavefunctions have maxima in this region. Based upon

these results it is not likely that a local approximation to the individual terms in the AI kernel is warranted.

In conclusion, our experience with Penning ionization (Chapter III) suggests that nuclear motion does play a role in the electron emission process; this emission is caused by the imaginary part of the kernel, and any local approximation to this quantity will undoubtedly be a poor one. For AI an analysis of the terms in the imaginary part of the kernel suggest that a local approximation will be likewise inappropriate.

We will now direct our attention to a method of solution of an inhomogeneous differential equation for Penning and associative ionization with a complex, separable kernel. Recalling that the p.v. contribution to the kernel may be approximated in a local manner and combined with the initial channel potential V_d, simplifications arising from an imaginary, non-local kernel will also be discussed.

IV.2 Method of Solution

Before proceeding with a method of solution of (2.58) it is of interest to point out a simplification which results from our formulation of the effective Hamiltonian problem in Chapter II. We had obtained an inhomogeneous second-order ordinary differential equation (ODE) by making a spectral decomposition of the operator $g^+(E)$ in

terms of heavy particle functions for PI and AI; this choice ensures a separable potential. Had we used the closed form for the radial Green's function (Micha, 1976) we would have likewise obtained a separable potential but for an inhomogeneous integro-differential equation (IDE) for the heavy particle wavefunction. A non-iterative solution of the latter requires that one solve a homogeneous IDE plus one (or more) particular inhomogeneous IDE. In the present approach we will see that we will be required to solve a homogeneous second-order ODE plus a collection of inhomogeneous ODE's; the construction of the kernel appears simpler with the present formulation.

Our method of solution of the non-local potential problem for complex potentials is in the spirit of the work of Gordon (1970) and Percival (as communicated by Marriott (1958)). We first review the method for real kernels to establish notation.

Consider the radial equation

$$D(R)f(R) = \int (R_1, R_2) \, dR' \, K(R,R')f(R')$$

(4.13)

where

$$D(R) = [d^2/dR^2 + (2M/\hbar^2)(E-V(R)) - L(L+1)/R^2]$$ (4.14)

and where we have suppressed energy and partial wave arguments for clarity. For a separable kernel

$$K(R,R') = \sum(i=1,N) \, V_i(R)W_i(R')$$

(4.15)

then

$$Df = \Sigma(i) \ V_i \ <W_i|f>$$

$$(4.16)$$

where $< \ | \ >$ denotes an integral over R'. The quantities $<W_i|f>$ are constant, independent of R and so we have an inhomogeneous equation with a fixed functional form on the right hand side. First we solve

$$Dh = 0 \qquad (4.17)$$

and the set

$$DI_i = V_i \qquad (4.18)$$

for $i=1$ to N. Now the most general solution f can be written as a particular solution, which is a linear combination of the solutions I_i, plus any homogeneous solution (such as h):

$$f = h + \Sigma(i) \ C_i \ I_i \ . \qquad (4.19)$$

It is readily shown by substitution of (4.19) into (4.16) that the coefficients $\{C_i\}$ satisfy the set of simultaneous linear equations (in matrix notation)

$$(1 - M_1)C = M_2 \qquad (4.20)$$

where 1 is the unit matrix of dimension N, C is the vector of coefficients, the matrix M_1 is given by

$$(M_1)_{ij} = <W_i|I_j> \qquad (4.21)$$

and M_2 is the vector

$$(M_2)_i = \langle W_i | h \rangle . \qquad (4.22)$$

The solution h is easily obtained: it is just the one-dimensional analog of the solution to the matrix Schrödinger equation discussed in Chapters I and III. For the inhomogeneous solutions the reader is directed to Gordon (1970) where a piecewise-analytic method for obtaining solutions such as I_i is discussed.

For the case of a complex, separable kernel we write again

$$D(R)f(R) = \int (0,\text{inf}) \, dR' \, K(R,R')f(R') \qquad (4.23)$$

but now for K we choose the expression

$$K(R,R') = \sum (i=1,2N) \, V_i(R) W_i(R') \qquad (4.24)$$

where V_i and W_i are real for i=1 to N; for i=N+1 to 2N we choose V_i real and make W_i imaginary. As before we solve

$$Dh = 0 \qquad (4.25)$$

and

$$DI_i = V_i \qquad (4.26)$$

for i=1 to 2N. By specifying W_i rather than V_i to be imaginary for i=N+1 to 2N those solutions I_i can all be real if we choose K-matrix boundary conditions as in

Chapter I. We write again

$$f = h + \Sigma(i=1,2N) \; C_i \; I_i \qquad (4.27)$$

and, as before, the $\{C_i\}$ satisfy

$$(1 - M_1)C = M_2 \qquad (4.28)$$

where now the matrices 1 and M_1 (4.21) and the vector M_2 (4.22) are of dimension 2N. Since some elements in M_2 can now be imaginary, the solutions C are in general complex. A substantial simplification has been achieved in this formulation: by making W_i be the imaginary part of the kernel for i=N+1 to 2N we have deferred operations involving complex arithmetic until the last step (4.28). Had we chosen to make V_i (i=N+1 to 2N) imaginary, the inhomogeneous solutions to (4.26) would be complex.

We now proceed to apply the above method to the homogeneous ODE discussed in the previous section. Inspection of the AI part of the kernel (2.57) allows us to write (suppressing energy arguments and partial wave indices for clarity)

$$K^{AI} = \Sigma(n=1,N) \; u_n v_n + \Sigma(m=1,N) \; w_m x_m \qquad (4.29)$$

with the identifications

$$u_n = \Psi(E^n, R) * (R\text{-dependent part of p.v.}) \tag{4.30a}$$

$$v_n = \Psi(E^n, R') * (R'\text{-dependent part of p.v.}) \tag{4.30b}$$

$$w_m = \Psi(E-E^m, R) V_{dE'''}(R) \tag{4.30c}$$

$$x_m = \Psi(E-E^m, R') (-i\pi) V_{E'''d}(R') \tag{4.30d}$$

$(E''' = E-E^m)$ or, combining in a single sum

$$K^{AI} = \Sigma(p=1, 2N) \ U_p V_p \tag{4.31}$$

where

$$U_p = u_p \tag{4.32a}$$

$$V_p = v_p \tag{4.32b}$$

for p=1 to N and

$$U_p = w_{p-N} \tag{4.32c}$$

$$V_p = x_{p-N} \tag{4.32d}$$

for p=N+1 to 2N.

For K^{PI} we make a quadrature approximation to the integral over E': using N' points,

$$K^{PI} = \int dE' \ K(E') = \Sigma(r=1, N') \ K_r(E_r) z_r$$

$$= \Sigma(r=1,N') \ K'_r(E_r) \tag{4.33}$$

where $\{z_r\}$ are quadrature weights which in the last line have been absorbed into K'_r. Now K^{PI} has been brought to the form

$$K^{PI} = \Sigma(r=1,N') \ a_r b_r \ + \Sigma(s=1,N') c_s d_s \tag{4.34}$$

where

$$a_r = \Psi(E_r,R)*(R\text{-dependent part of p.v.}) \tag{4.35a}$$

$$b_r = \Psi(E_r,R')*(R'\text{-dependent part of p.v.}) \tag{4.35b}$$

$$c_s = \Psi(E-E_s,R) V_{dE''}(R) \tag{4.35c}$$

$$d_s = \Psi(E-E_s,R')(in) V_{E''d}(R') \tag{4.35d}$$

$(E'' = E-E_s)$ or

$$K^{PI} = \Sigma(q=1,2N') \ A_q B_q \tag{4.36}$$

with the identification

$$A_q = a_q \tag{4.37a}$$

$$B_q = b_q \tag{4.37b}$$

for q=1 to N' and

$$A_q = c_{q-N'} \tag{4.37c}$$

$$B_q = d_{q-N'} \qquad (4.37d)$$

for q=N'+1 to 2N'.

We now have the result

$$K = \Sigma(p=1,2N) \ U_p V_p \ + \ \Sigma(q=1,2N') \ A_q B_q \qquad (4.38)$$

or

$$K = \Sigma(t=1,T) \ F_t G_t \qquad (4.39)$$

where

$$T = 2N + 2N' \qquad (4.40)$$

and

$$F_t = U_t \qquad (4.41a)$$

$$G_t = V_t \qquad (4.41b)$$

for t=1 to 2N, and

$$F_t = A_t \qquad (4.41c)$$

$$G_t = B_t \qquad (4.41d)$$

for t=2N + 1 to T. With some effort we have been able to put the kernel for AI and PI into a form (4.39) such as (4.24) which we can solve in exactly the same manner. Obtain the solutions to

$$D h = 0 \qquad (4.42)$$

$$DI_t = F_t \qquad (4.43)$$

for t=1 to T. Then the solution X of the inhomogeneous differential equation

$$DX = \int KX \qquad (4.44)$$

$$= \Sigma(t=1,T) \; F_t \; <G_t \; |X>$$

is given as

$$X = h + \Sigma(t=1,T) \; I_t \; Y_t \qquad (4.45)$$

and the coefficients $\{Y_t\}$ are the solution to the matrix

equation

$$(1 - M_1)Y = M_2 \qquad (4.46)$$

where the unit matrix, M_1 and M_2 are of dimension T.

Specifically,

$$(M_1)_{ij} = <G_i \; |I_j > \qquad (4.47)$$

$$(M_2)_i = <G_i \; |h> . \qquad (4.48)$$

The expression (4.45) for the solution of (4.44) is the main result of this section. The functions G_i are either real or imaginary, and the solutions I_i are real; thus the elements of M_1 and M_2 are either real or imaginary, but not complex. As we found above, we are able to defer any arithmetic operations involving complex numbers until the very last step (4.46), the solution of the set of linear equations which determine the coefficients. Although this last point is not critical to the mathematical development, it is certainly of practical importance when

doing machine computation: manipulations directly in terms of complex quantities exact an appreciable expenditure of time due to the increased number of arithmetic operations required.

In light of the discussion in the previous section regarding approximations to the full kernel, in those cases where we may either neglect the principal-value contributions or where a local approximation may be made to the real part of the kernel, the following simplifications are noted: the quantities u_n , v_n , a_r and b_r are absent, and the dimensionality of our matrix problem is reduced by a factor of two (now $T = N + N'$). M_1 and M_2 are composed of imaginary elements, and in this case the complex coefficients Y_i can be obtained by solving a <u>real</u> set of simultaneous linear equations.

This concludes our discussion of a method for the (in principle) exact solution of an inhomogeneous differential equation arising from a theory of ionizing collisions between atoms. Once we have constructed the homogeneous solution h and the particular solutions I_i , the M arrays can be calculated and the desired scattering solution obtained algebraically. In the last section we will summarize the principal results of the present work and

discuss problems where further studies are warranted.

IV.3 Discussion

Our study of ionizing atomic collisions at low energies has caused us to focus on both electronic and heavy-particle dynamic aspects. The electronic portion of the problem concerns the description of the appropriate electronic wavefunctions, potential energy curves and coupling matrix elements. Discussion was given of the construction of a continuum orbital using the expansion method of Harris (1967) which has enjoyed widespread application for electron-atom scattering. Continuum electronic wavefunctions are then built up from ground state molecular ion wavefunctions and these continuum orbitals. We also proposed how to obtain molecular resonance or "hole" wavefunctions; a resonance wavefunction which is explicitly orthogonal to the continuum electronic functions was obtained by projection operator techniques. Alternatively, an approximate resonance wavefunction was obtained from a ground state function by the appropriate single-particle excitation; this function was then orthogonalized to the continuum electronic functions to give an orthogonal basis of electronic wavefunctions suitable for our scattering problem.

We made a detailed numerical investigation of Penning ionization of Ar by He*($1s2s, ^3S$) using a coupled-channels formalism (Bellum and Micha, 1978) for the heavy particle wavefunctions. Detailed analysis of the energy distribution of the emitted electron suggested a profound effect of nuclear motion on the ionization probability. Appreciable enhancement of this energy-differential cross section was found to occur at energies corresponding to at least one heavy particle quasibound state and perhaps several "discrete states in the continuum" of nuclear motion. This led us to propose that the initial electronic state undergoes a transition to an intermediate state resembling an electron loosely bound to an ionic core; it is from this intermediate that the electron may then be ejected. A method was described whereby these "discrete" continuum heavy particle states could be obtained by applying basis set expansion techniques to the scattering states as well as to the bound states of nuclear motion.

The validity of approximating the full matrix Schrödinger equation in a coupled channels theory by a collection of two-state scattering equations was demonstrated by exploring alternative computational techniques; here we chose to solve the Riccati transform of the matrix Schrödinger equation using a method which afforded a significant reduction in computer time. The

decoupling approximation was found to be independent of energy and heavy particle angular momentum partial wave over the range of energy of interest. Penning ionization cross sections were obtained and found to compare favorably with experimental results at energies from 20-100 meV.

In Chapter II an effective Hamiltonian theory was developed for collisional ionization along the lines of Feshbach's unified theory of nuclear reactions (1958; 1962). Using projection operator techniques we derived an effective potential for the colliding particles which was complex, non-local and energy-dependent. In Chapter IV a detailed analysis was made of the Penning and associative ionization contributions to the kernel of a inhomogeneous, second-order ordinary differential equation. We demonstrated that although the real part of the kernel may by simplified by a local approximation, it was inappropriate to similarly treat the imaginary part. We also discussed formation of long-lived nuclear motion states in the final channel and suggested that their lifetimes be determined so that they may be correctly classified as PI or AI; this classification of course depends upon an experimental detection time. A method was developed for the solution of such inhomogeneous equations with complex kernels; the method is general, and we discussed its implementation for PI and AI and pointed out

simplifications resulting from the case of a purely imaginary kernel. A particular advantage of the formulation defers any operations involving complex quantities until the final step, which would have practical consequences for an actual computation.

There are still many interesting aspects of collisional ionization which merit further attention. For example, extension of either the coupled channels or effective Hamiltonian theory to include higher angular momentum partial waves for the ejected electron is desirable. Although limiting the treatment here to the l=0 electron partial wave is advantageous from the point of view of simplifying the study of nuclear dynamics, higher partial waves of course must contribute. A further improvement of either theory would be the inclusion of multiple electronic continua. For the He*-Ar system studied here, there is a $^2\pi$ molecular ion electronic state which may also be formed. This feature gives rise to interference effects: the initial discrete state is now coupled to two continuum electronic states, and there are in principle couplings between the two continua as well as within each continuum.

From the computational point of view, we mentioned in Chapter III that, in addition to final channel heavy particle resonance effects, initial channel quasibound states may modify the dynamics at lower collision

energies. It would be of interest to see whether the cross section rises at much lower energies and if such a rise could be explained by resonance behavior. A more exciting prospect is the implementation of the method for solving inhomogeneous equations for complex kernels as detailed in this chapter. The solution requires homogeneous and inhomogeneous solutions as input, and these may be obtained by standard methods. Application to an analytically solvable two-state scattering problem would be a first step toward demonstrating its feasibility and in affording comparisons with traditional coupled-channels treatments.

Table 2

HeAr(+) Bound Levels

E (1/cm)

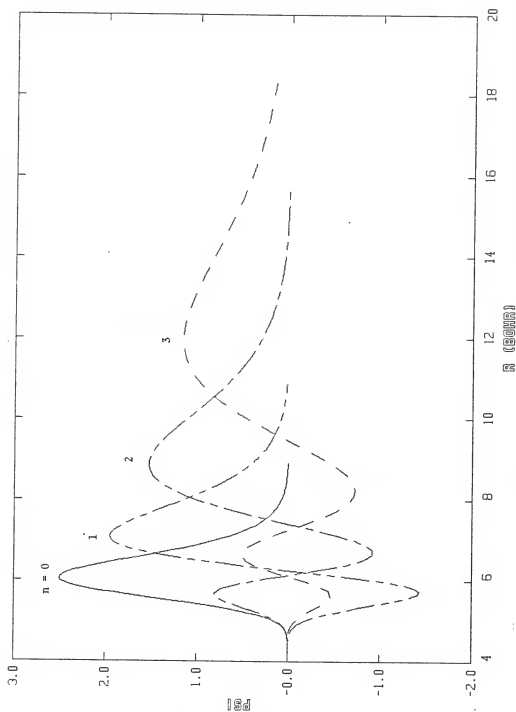| L	n=0	n=1	n=2	n=3	n=4	n=5
0	-1.409(2)	-5.048(1)	-1.637(1)	-4.182	-5.73(-1)	-8.8(-3)
1	-1.400(2)	-4.978(1)	-1.591(1)	-3.913	-4.608(-1)	
2	-1.382(2)	-4.838(1)	-1.499(1)	-3.386	-2.533(-1)	
3	-1.356(2)	-4.629(1)	-1.363(1)	-2.670	a	
4	-1.320(2)	-4.352(1)	-1.183(1)	-1.652		
5	-1.276(2)	-4.007(1)	-9.633	-5.400(-1)		
6	-1.223(2)	-3.597(1)	-7.066			
7	-1.162(2)	-3.122(1)	-4.182			
8	-1.091(2)	-2.586(1)	-1.061			
9	-1.012(2)	-1.992(1)	a			
10	-9.250(1)	-1.343(1)				
11	-8.293(1)	-6.456				
12	-7.252(1)	a				
13	-6.128(1)	a				
14	-4.924(1)	a				
15	-3.641(1)					
16	-2.286(1)					
17	-8.448					
18	a					
19	a					

----

a = quasibound level

Table 3

HeAr(+) Quasibound Levels

n	L	E (1/cm)	Width (1/cm)	Lifetime (sec)
0	18	6.634	3.5(-20)	1.5(8)
	19	2.240(1)	4.2(-12)	1.3
1	12	9.190(-1)	5.4(-19)	9.8(6)
	13	8.540	2.1(-8)	2.5(-4)
	14	1.609(1)	2.6(-6)	2.0(-6)
2	9	2.138	4.0(-8)	1.3(-4)
4	3	2.30 (-3)	2.4(-12)	2.2

Figure 11 Vibrational Wavefunctions for n=0,1,2,3
Levels of HeAr+ (L=0)

129

HERM(+) WFNS (N=0,1,2,3)

INEN, McIntosh Plot System - Mexico   11/04/80   23.18.00

Figure 12 Vibrational Wavefunctions for n=4,5 Levels
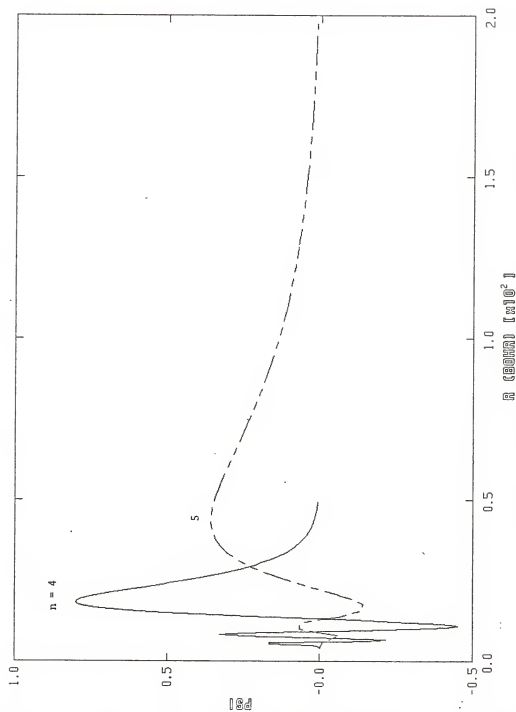of HeAr+ (L=0)

HEAR(+) WFNS (N=4,5)

n = 4

5

PSI

R (BOHR) [*10²]

1.0   0.5   -0.0   -0.5

0.0   0.5   1.0   1.5   2.0

INEN: McIntosh Plot System - Mexico   11/04/80   23.18.02

Figure 13 Imaginary Part of Associative Ionization
Kernel for n=0 Level of HeAr$^+$ (L=0)

IM K 0 (R,RP)

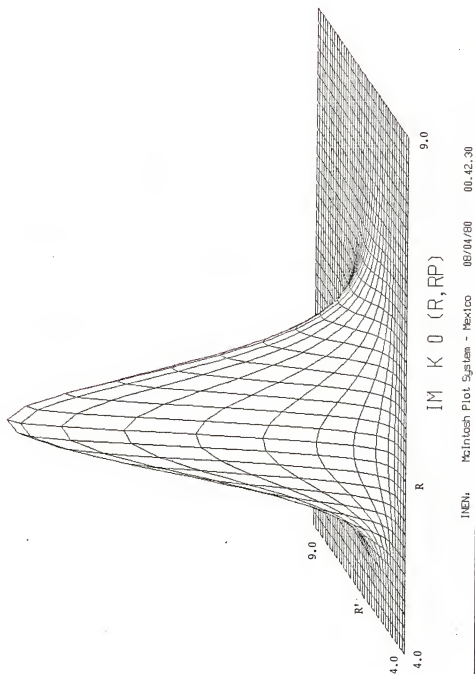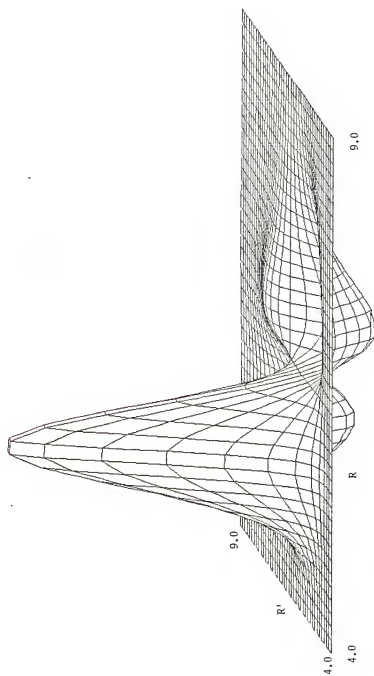INEN, Macintosh Plot System - Mexico   08/04/80   00.42.30

Figure 14 Imaginary Part of Associative Ionization
Kernel for n=1 Level of HeAr⁺ (L=0)

135

IM K 1 (R,RP)

INEN: McIntosh Plot System - Mexico   08/04/80   00.43.25

Figure 15 Imaginary Part of Associative Ionization
Kernel for n=2 Level of HeAr$^+$ (L=0)

IM K 2 (R,RP)

R

R'

4.0

4.0

9.0

9.0

INEN: McIntosh Plot System - Mexico   08/04/80   00.43.49

Figure 16 Imaginary Part of Associative Ionization
Kernel for n=3 Level of HeAr$^+$ (L=0)

139
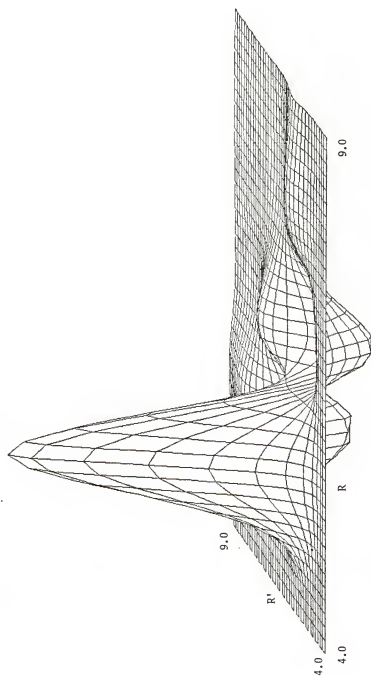

IM K 3 (R,RP)

INEN, McIntosh Plot System - Mexico 08/04/80 00.44.05

Figure 17   Imaginary Part of Associative Ionization
Kernel for n=4 Level of HeAr⁺ (L=0)

IM K 4 (R,RP)

R'

R

9.0

9.0

4.0

4.0

IMEN.   McIntosh Plot System - Mexico   08/04/80   00.44.35
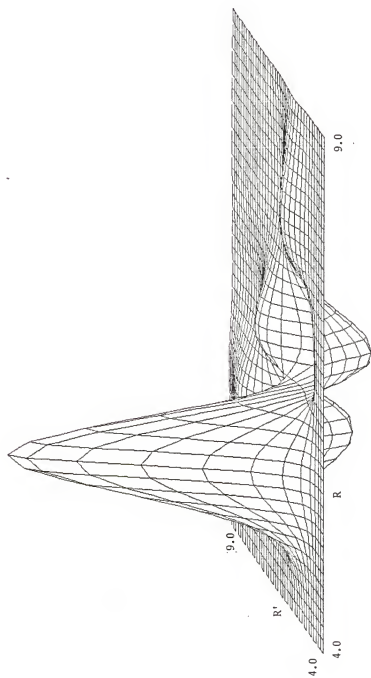
Figure 18 Imaginary Part of Associative Ionization
           Kernel for n=5 Level of HeAr+ (L=0)
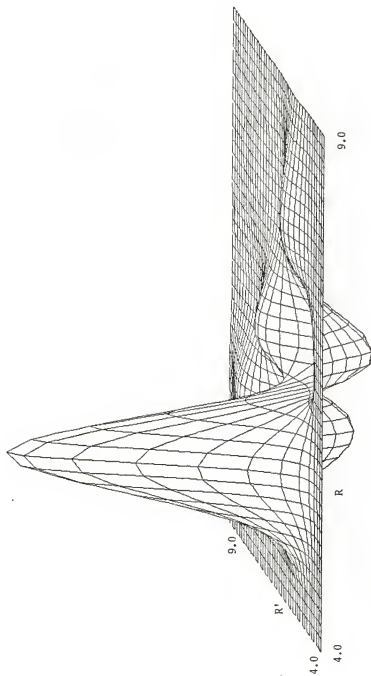
IM K 5 (R,RP)

IMEN.   McIntosh Plot System - Mexico   08/04/80   00.45.09
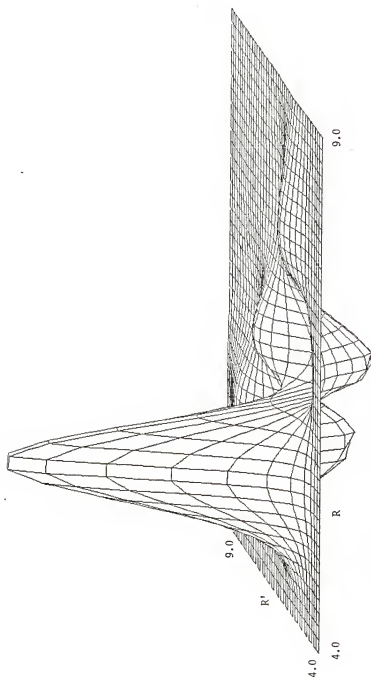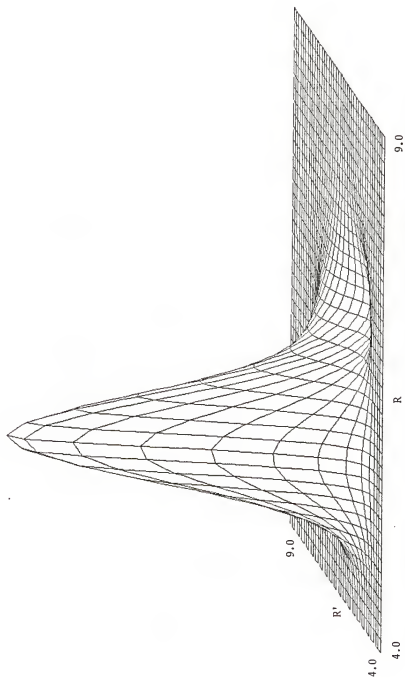
Figure 19 Imaginary Part of Associative Ionization
Kernel for n=0-5 Levels of HeAr$^+$ (L=0)

IM SUM K (R,RP)

INEN, McIntosh Plot System - Mexico 08/04/80 00.47.12

APPENDIX A
INTERACTION POTENTIALS AND COUPLINGS

For convenience the potentials used in the work of Relyea and Micha (1979) and Bellum and Micha (1978) are reproduced below. To give a simple functional form to the potentials for HeAr* and HeAr⁺ they have both been represented by a Born-Mayer exponential repulsion plus a long-range van der Waals attractive tail. They can be represented by

$$V(R) = Ae^{-R/a} + f(R;R^0,b,c)\,V_{LR}(R) \qquad (A.1)$$

where f is the 3-parameter switching function of Eckart (1930)

$$f(R;R^0,b,c) = (1 + e^{(R-R^0)/c})^{-1} *$$
$$\{1 + b(1 + e^{(R-R^0)/c})^{-1}\} \qquad (A.2)$$

which takes on the values $(0,1)$ at the endpoints of the interval $(0,\infty)$ of R, and which exhibits a local maximum (for b>0) at

$$R_{max} = R^0 + c*\ln[\,(b+1)/(b-1)\,] . \qquad (A.3)$$

The switching function is used to smoothly join the repulsive and attractive parts of the potential, with

parameters determined by reproducing the well-depth and position of the potential minimum. To determine R^0 the value of R_{max} was chosen to coincide with the position R_m of the potential minima. The Born-Mayer parameter a is deduced from the MSX$_\alpha$ results of Bellum and Micha (1977) on HeAr* and HeAr+; the value of c is set equal to a. To determine A and b we use the conditions

$$V(R_m) = -E_m \qquad (A.4)$$

$$V'(R_m) = 0$$

where E_m is the well depth. For HeAr* the values of E_m and R_m are those of Chen et al. (1974); those relevant to HeAr+ are from Nakamura (1975). Specifically, we obtain (energies in Hartrees, R in Bohr)

$$V_{HeAr*} = 4.39678e^{-R/0.9675} + f(R;9.4488,2.81505,0.9675)$$

$$*(-226.0/R^6) \qquad (A.5)$$

and

$$V_{HeAr+} = 44.6527e^{-R/0.532} + f(R;5.936,6.42317,0.532)$$

$$*(-0.6904/R^4-7.94/R^6) . \qquad (A.6)$$

The coefficient of R^{-6} for HeAr* is from Bell et al. (1968); for HeAr+ we use the R^{-4} coefficient of Dalgarno (1962) and the R^{-6} coefficient of Nakamura (1975).

The coupling matrix element $V_{d\varepsilon}(R)$ has been parametrized in terms of an autoionization width

$$\gamma(R) = 2\pi \; |\langle \phi_d | H_{el} | \phi(\varepsilon) \rangle|^2 \qquad (A.7)$$

which is often given the exponential representation

$$\gamma(R) = A^0 e^{-R/a^0} \qquad (A.8)$$

in experimental and semiempirical analyses. To give the model coupling an explicit ε-dependence (which is absent in γ of (A.8)) it is noted that the normalization constant for a Coulomb orbital of energy ε is $(2/\pi k)^{1/2}$ where $k^2 = 2m\varepsilon/\hbar^2$ (m=electron mass). We write

$$\phi(\varepsilon) = (2/\pi k)^{1/2} \phi' \qquad (A.9)$$

and give the coupling matrix element $\langle \phi_d | H_{el} | \phi' \rangle$ an R-dependence suggested by (A.8). Thus

$$A^0 e^{-R/a^0} = 2\pi(2/\pi k)(A'e^{-R/a'})^2 \quad . \qquad (A.10)$$

Selection of A^0 and a^0 values from semiempirical analyses allows us to obtain values for A' and a' and the coupling becomes

$$V_{dC}(R) = (2/\pi k)^{1/2} A'e^{-R/a'} \quad . \qquad (A.11)$$

Tabulation of values of various workers may be found in Bellum and Micha (1978). For all work reported here, the values $A'=50.0$ Hartrees and $a'=0.7$ Bohr were used.

APPENDIX B

TRANSITION AMPLITUDES T_{QQ}, T_{PQ}

Recall we had written

$$(E - QHQ - QHEG_P^+PHQ)Q\Psi_Q^+ = 0$$

or

$$(E - H')Q\Psi_Q^+ = 0$$

where

$$H' = QHQ + QHPG_P^+PHQ = H_{QQ} + F^+$$

$$= |\phi_d>(T_R + V_d)<\phi_d| + F^+$$

$$= H^0 + V^0 + V^1$$

with the choice of Q as a projector onto the closed electronic channel,

$$Q = |\phi_d><\phi_d|$$

and where Ψ_Q is the total wavefunction (nuclear and electronic) when the initial channel is Q. We also remember that H_{QQ} accounts for elastic scattering in Q by potential V_d, and F^+ accounts for transitions into the P subspace (i.e., ionization) via interaction PHQ,

propagation in P via G_P^+, and a final interaction QHP which accounts for recombination in P and which returns the nuclei to their initial states in the entrance channel Q. The two-potential formalism (Rodberg and Thaler, 1967) for a potential $V = V^0 + V^1$, which requires eigenfunctions $|a\rangle$ of H^0, $|b\rangle$ of $H^0 + V^0$, and $|c\rangle$ of H' gives, for transitions from channel i to channel f,

$$T_{fi} = \langle a_f | V^0 | b_i^+\rangle + $$

$$\langle b_f^- | V^1 | c_i^+\rangle .$$

In our case we make the identifications (using the sub-index "q" to denote functions defined only within the Q subspace):

$$|a\rangle = |\Psi_q^0\rangle = |\phi_d\rangle|u^0\rangle$$

$$|b^+\rangle = |\Psi_q^+\rangle = |\phi_d\rangle|u^+\rangle$$

$$|c^+\rangle = |Q\Psi_Q^+\rangle$$

$$= |\phi_d\rangle\langle\phi_d|\Psi_Q^+\rangle$$

$$= |\phi_d\rangle|X_Q^+\rangle$$

and u^+ and u^0 are related by the Lippmann-Schwinger equation

$$u^+ = u^0 + G_{Q,0}^+ V_d u^+$$

with solution

$$u_q^+ = u_q^0 + G_Q^+ V_d u_q^0$$

and

$$G_Q^+ = (E - T_R - V_d + i\epsilon)^{-1}$$

and

$$G_{Q,0}^+ = (E - T_R + i\epsilon)^{-1} .$$

The last two quantities are related by

$$G_Q^+ = G_{Q,0}^+ + G_{Q,0}^+ V_d G_Q^+$$

$$= G_{Q,0}^+ + G_Q^+ V_d G_{Q,0}^+ .$$

We thus obtain

$$T_{QQ} = \langle \Psi_q^0 | \phi_d \rangle V_d \langle \phi_d | \Psi_q^+ \rangle$$

$$+ \langle \Psi_q^- | F^+ | Q \Psi_Q^+ \rangle$$

$$= \langle u_q^0 | V_d | u_q^+ \rangle + \langle \Psi_q^- | F^+ | Q \Psi_Q^+ \rangle .$$

Recalling

$$F Q \Psi_Q^+ = QHPG_P^+ PHQQ \Psi_Q^+ = QHP \Psi_Q^+$$

we obtain, alternatively,

$$T_{QQ} = \langle u_q^0 | V_d | u_q^+ \rangle + \langle \Psi_q^- | QHP | \Psi_Q^+ \rangle .$$

Note that the first term on the right-hand side is just the transition matrix element for elastic scattering in Q, uncoupled to P, so we write

$$T_{QQ} = T_{QQ}^0 + \langle \Psi_q^- | F^+ | Q \Psi_Q^+ \rangle$$

$$= T_{QQ}^{\ 0} + \langle \Psi_q^- | QHP | \Psi_Q^+ \rangle$$

where

$$T_{QQ}^{\ 0} = \langle u^0 | V_d | u^+ \rangle .$$

The distorted-wave Born approximation (DWB) amounts to replacement of eigenfunctions of H' by eigenfunctions of $H^0 + V^0$ so

$$Q\Psi_Q^+ \longrightarrow Q\Psi_q^+ = \Psi_q^+$$

and the first form of T_{QQ} becomes

$$T_{QQ}^{DWB,1} = T_{QQ}^{\ 0} + \langle \Psi_q^- | F^+ | \Psi_q^+ \rangle$$

and at this point coupling to the ionized channel is still present through the operator F^+.

In the second form of T_{QQ} using

$$P\Psi_Q^+ = \Psi_Q^+ - Q\Psi_Q^+$$

and the DWB approximation gives

$$T_{QQ}^{DWB,2} = T_{QQ}^{\ 0} + \langle \Psi_q^- | QH | \Psi_Q^+ \rangle$$
$$- \langle \Psi_q^- | QHQ | \Psi_q^+ \rangle .$$

For T_{PQ}, the ionization amplitude, we make use of

$$Q(E - H)Q\Psi_Q = QHP\Psi_Q$$

$$P(E - H)P\Psi_Q = PHQ\Psi_Q$$

and the corresponding homogeneous equations

$$Q(E - H)Q\psi_q = 0$$

$$P(E - H)P\psi_p = 0$$

to write the channel Hamiltonians

$$H_Q = QHQ + QHP = H^0 + V$$

and

$$H_P = PHP + PHQ = H^{0'} + V' .$$

Then using

$$T_{fi} = \langle\psi_f^-|V'|\psi_i^+\rangle$$

gives

$$T_{PQ} = \langle\psi_p^-|PHQ|\psi_Q^+\rangle .$$

The DWB approximation here gives directly

$$T_{PQ}^{DWB} = \langle\psi_p^-|PHQ|\psi_q^+\rangle$$

so again we need not determine ψ_Q or its P or Q

projections. This approximation retains states fully

distorted by elastic scattering in Q and P (ψ_q^+ and ψ_p^-,

resp.) and is superior to the normal Born approximation to

T_{PQ} which replaces $Q\psi_Q^+$ by ψ_q^0, a free-motion wavefunction

(an eigenfunction of H^0) which is not distorted by elastic

scattering by V_d in Q space.

APPENDIX C
DERIVATION OF THE LOG-DERIVATIVE ALGORITHM

Consider the radial equation

$$u''(r) + q(r)*u(r) = 0 \qquad (C.1)$$

where

$$q(r) = (2m/\hbar^2)(E - V_{eff}(r))$$

or

$$q(r) = k^2 - U(r)$$

and where

$$V_{eff}(r) = v(r) + (\hbar^2/2m)l(l+1)/r^2$$

For p a positive, real number write (Johnson, 1973)

$$u''(r) - p^2 u(r) = -(q(r) + p^2)u(r) \qquad (C.2)$$

or

$$u''(r) - p^2 u(r) = - f(r)u(r) \qquad (C.3)$$

where

$$f(r) = q(r) + p^2 \qquad (C.4)$$

Consider also the corresponding homogeneous equation

$$w''(r) - p^2 w(r) = 0$$

Then the solution to (C.1) can be written as

$$u(r) = e^{pr} + 1/(2p) \int (0,inf) e^{-p(r-r')} f(r')u(r')dr' \qquad (C.5)$$

Let

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$$F(r) = f(r) * u(r) \qquad (C.6)$$

then

$$u(r) = e^{pr} + 1/(2p) \int (0, inf) \, e^{-p(r-r')} F(r') \, dr' \qquad (C.7)$$

and

$$\lim_{r \to inf} u(r) =$$

$$e^{pr} + 1/(2p) e^{-pr} \int (0, inf) \, e^{pr'} F(r') \, dr' \qquad (C.8)$$

Let

$$K = \int (0, inf) \, e^{pr} F(r) \, dr \qquad (C.9)$$

Then

$$\lim_{r \to inf} u(r) = e^{pr} + 1/(2p) e^{-pr} K \qquad (C.10)$$

Multiply (C.5) by $f(r)$; then

$$F(r) = f(r) e^{pr} + 1/(2p) \int (0, inf) \, e^{-p(r-r')} f(r) F(r') \, dr' \qquad (C.11)$$

Our objective is to obtain (C.10), with K given by (C.9) and $F(r)$ by (C.11). Perform the integrals in (C.9) and (C.11) numerically, using $N-1$ points $r(j)$ and weights $c(j)$. So

$$K_1 = \Sigma(j=1, N-1) \, e^{pr(j)} F_1(r(j)) c(j) \qquad (C.12)$$

and

$$F_1(r(i)) = f(r(i)) e^{pr(i)} + 1/(2p) \, \Sigma(j=1, N-1) \, f(r(i))$$

$$*e^{-p(r(i)-r(j))} *F_1(r(j))c(j) \tag{C.13}$$

Now repeat, using N points and weights:

$$K = \Sigma(j=1,N) \ e^{pr(j)} F(r(j))c(j) \tag{C.14}$$

and

$$F(r(i)) = f(r(i))e^{pr(i)} +$$

$$1/(2p)\Sigma(j=1,N) f(r(i)) e^{-p(r(i)-r(j))} F(r(j))c(j) \tag{C.15}$$

Consider (C.15) at $r=r(N)$:

$$F(r(N)) = f(r(N)) + 1/(2p) f(r(N)) F(r(N)) c(N) +$$

$$1/(2p)\Sigma(j=1,N-1) f(r(N)) e^{-p(r(N)-r(j))} F(r(j))c(j) \tag{C.16}$$

and then

$$F(r(N)) = \tag{C.17}$$

$$(\ f(r(N))e^{pr(N)} + 1/(2p) \ \Sigma(j=1,N-1) \ f(r(N))*$$

$$e^{-p(r(N)-r(j))} F(r(j))c(j) \ ) * (1-1/(2p) f(r(N))c(N)^{-1}$$

so

$$F(r(N)) = -2p/c(N)e^{pr(N)} A-1/c(N) A \Sigma(j=1,N-1) \ F(r(j))c(j)$$

$$*e^{-p(r(N)-r(j))} \tag{C.18}$$

where

$$A=1/(2p)f(\ r(N))c(N)*(1/(2p) f(r(N))c(N) \ -1)^{-1} \tag{C.19}$$

Thus we can write

$$F(r(N)) = -2p/c(N)e^{pr(N)} A - 1/c(N)Ae^{-pr(N)} b \tag{C.20}$$

with b to be determined.

We now assert that for i<N, $F(r(i))$ is related to $F_1(r(i))$ by

$$F(r(i)) = F_1(r(i))a \qquad (C.21)$$

with a to be determined. Substitution of (C.20) and (C.21) into (C.15),

$$F_1(r(i))a = f(r(i))e^{pr(i)} + 1/(2p)f(r(i)) \sum(j=1,N-1) ac(j)$$

$$*e^{-p(r(i)-r(j))} F_1(r(j)) + 1/(2p)f(r(i))e^{-p(r(i)-r(N))} *$$

$$(-2p/c(N)e^{pr(N)} A - 1/c(N)Ae^{-pr(N)} b)c(N) \qquad (C.22)$$

followed by substitution of (C.13) into the left-hand side of (C.22) leads to

$$(f(r(i))e^{pr(i)} +1/(2p)\sum(j=1,N-1) f(r(i))e^{-p(r(i)-r(j))} \qquad (C.23)$$

$$*F_1(r(j))c(j))a = f(r(i))e^{pr(i)} + 1/(2p)f(r(i))$$

$$*\sum(j=1,N-1) e^{-p(r(i)-r(j))} F_1(r(j))ac(j) + 1/(2p)*f(r(i))$$

$$*e^{-p(r(i)-r(N))} (-2p/c(N)e^{pr(N)} A-1/c(N)Ae^{-pr(N)} b)c(N)$$

Simplifying, we get

$$f(r(i))e^{pr(i)} a=f(r(i))e^{pr(i)} -f(r(i))e^{-p(r(i)-r(N))} *$$

$$e^{pr(N)} A - 1/(2p)f(r(i))e^{-p(r(i)-r(N))} Abe^{-pr(N)} \qquad (C.24)$$

This holds for all $r(i)$, so that at $r(i)=r(N)$:

$$a = 1 - A - 1/(2p) Abe^{-2pr(N)} \qquad (C.25)$$

Now we obtain b; substitute (C.21) and (C.20) into (C.15) for $r(i)=r(N)$:

$$-2p/c(N)e^{pr(N)} A - 1/c(N)Ae^{-pr(N)} b=f(r(N))e^{pr(N)} \qquad (C.26)$$

$$+ 1/(2p) \sum_{(j=1,N-1)} f(r(N))e^{-p(r(N)-r(j))} F_1(r(j))ac(j)$$

$$+1/(2p)f(r(N))(-2p/c(N)e^{pr(N)}A-1/c(N)Ae^{-pr(N)}b)c(N)$$

and for $r(N) > r(j)$ we obtain

$$-2p/c(N)e^{pr(N)} A - 1/c(N)Ae^{-pr(N)} b=f(r(N))e^{pr(N)} +$$

$$1/(2p)f(r(N))e^{-pr(N)} K_1 a-f(r(N))(e^{pr(N)} A +$$

$$1/(2p)e^{-pr(N)} Ab) \qquad (C.27)$$

Simplifying (C.27):

$$A(e^{pr(N)}+1/(2p)e^{-pr(N)} b)(-2p/c(N)+f(r(N))) =$$

$$f(r(N))(e^{pr(N)}+1/(2p)e^{-pr(N)} K_1 a) \qquad (C.28)$$

Note that

$$-2p/c(N) + f(r(N)) = f(r(N))/A$$

so that

$$b=K_1 a \qquad (C.29)$$

Now express K (C.14) in terms of K_1 (C.12):

$$K = \sum(j=1, N) \ e^{pr(j)} \ F(r(j)) c(j)$$

$$= \sum(j=1, N-1) \ e^{pr(j)} \ F_1(r(j)) ac(j) + e^{pr(N)} \ F(r(N)) c(N)$$

$$= K_1 a + e^{pr(N)} c(N) (-2p/c(N) e^{pr(N)} A - 1/c(N) e^{-pr(N)} Ab)$$

$$= K_1 a - 2pe^{2pr(N)} A - Ab$$

or

$$K = b - 2pe^{2pr(N)} A - Ab \qquad (C.30)$$

Keeping in mind the results (C.25), (C.29) and (C.30), define

$$b' = -1/(2p) \ e^{-2pr(N)} \ b \qquad (C.31)$$

$$K_2 = -1/(2p) \ e^{-2pr(N)} \ K \qquad (C.32)$$

$$K_3 = -1/(2p) \ e^{-2pr(N-1)} \ K_1 \qquad (C.33)$$

or

$$K_1 = -2pe^{2pr(N-1)} \ K_3$$

$$= -2pe^{2pr(N)} \ e^{-2ph} \ K_3 \qquad (C.33)$$

where $h = r(N) - r(N-1)$. Then (C.25) becomes

$$a = 1 - A + Ab' = 1 + A(b' - 1) \qquad (C.34)$$

(C.29) becomes

$$b' = e^{-2ph} K_3 a \tag{C.35}$$

and (C.30) becomes

$$K_2 = b' + A - Ab' = A + b'(1-A) \tag{C.36}$$

Also define

$$K_4 = e^{-2ph} K_3 \tag{C.37}$$

so that

$$b' = K_4 a \tag{C.38}$$

Substitute (C.34) into (C.38) to obtain

$$b' = (1 - K_4 A)^{-1} K_4 (1-A) \tag{C.39}$$

Substitution of (C.39) into (C.36) gives

$$K_2 = A + (1 - K_4 A)^{-1} K_4 (1-A)^2 \tag{C.40}$$

From (C.10) we can now write, at $r = r(N)$,

$$u(r(N)) = e^{pr(N)} + 1/(2p) e^{-pr(N)} (-2pe^{2pr(N)} K_2)$$

$$= e^{pr(N)} (1 - K_2) \tag{C.41}$$

Differentiating (C.10) with respect to r gives

$$u'(r) = pe^{pr} + 1/(2p)(-p) e^{-pr} K$$

$$= pe^{pr} + p(-1/(2p) e^{-pr} K)$$

which becomes, at $r = r(N)$,

$$u'(\mathfrak{r}(N)) = pe^{pr(N)}(1+K_2)$$

$$(C.42)$$

Define $L(\mathfrak{r})$, the reciprocal of the logarithmic derivative, by

$$L(\mathfrak{r}) = u(\mathfrak{r})(u'(\mathfrak{r}))^{-1}$$

$$= (1-K_2)(p(1+K_2))^{-1} \qquad (C.43)$$

From (C.19),

$$\lim_{p \to 0} A = 1$$

and by (C.36) then

$$\lim_{p \to 0} K_2 = 1$$

Let

$$Z = (1-K_2)/(2p) \qquad (C.44)$$

so

$$\lim_{p \to 0} Z = L$$

Also define Z' by

$$K_3 = 1 - 2pZ' \qquad (C.45)$$

then

$$-Z = -(1-K_2)/(2p)$$

$$= (1-A)-(1-K_2 A)^{-1} K_2 (1-A)^2/(-2p) \qquad (C.46)$$

and

$$(1-A)/(-2p) = -1/(2p)(1-(f(\mathfrak{r}(N))c(N))(f(\mathfrak{r}(N))c(N)-2p)^{-1}$$

$$= (f(\mathfrak{r}(N))c(N)-2p)^{-1}$$

Now expand K_4 in powers of p, keeping terms through first order:

$$K_4 = e^{-2ph} K_3$$

$$= (1-2ph)(1-2pZ')$$

$$= 1-2p(h+Z')$$

Then

$$1-K_4 A = (f(r(N)c(N)-2p-(1-2p(h+Z'))f(r(N)c(N))$$

$$* (f(r(N)c(N)-2p)^{-1} \tag{C.47}$$

and after straightforward but tedious algebra we arrive at

$$Z=(h+Z'+2p(h+Z')/(f(r(N)c(N))(-1+2p/f(r(N)c(N))^{-1}$$

$$*(1-f(r(N)c(N)(h+Z'))^{-1} \tag{C.48}$$

and

$$\lim_{p-->0} Z = L = (h+Z')(1-q(r(N))c(N)(h+Z'))^{-1} \tag{C.49}$$

and now

$$Z=(h+Z')(1-q(r(N))c(N)(h+Z'))^{-1} \tag{C.50}$$

Finally, let

$$y(i)=z(i)^{-1} \tag{C.51}$$

and we obtain the result

$$y(i)=(hy'+1)^{-1}y'-q(r(i))c(i) \tag{C.52}$$

where $y'=y(i-1)$ and $y(k)=y(r(k))$. We could at this point take $c(i)$ to be Simpson's rule weights, i.e.,

$$c(i) = h/3 \text{ at } y=y(0) \text{ and } y=y(N),$$

$$= 4h/3 \text{ at } y=y(1),y(3),\ldots,y(N-1),$$

$$= 2h/3 \text{ at } y = y(2), y(4), \ldots, y(N),$$

where N=even integer. Equation (C.52) is the log derivative algorithm presented by Johnson (1973), and additional discussion on the choice of $c(i)$ can be found in Johnson and Secrest (1966; 1968).

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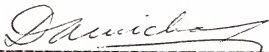Shore, B. W., J. Chem. Phys. 63, 3835 (1975).

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Lawrence Ralph Relyea was born September 20, 1951, in Schenectady, New York. He attended public schools in Colonie, New York, until graduating from Colonie Central High School in 1969. From 1969 until 1973 he attended St. Lawrence University in Canton, New York, where he received his B.S. degree in chemistry _cum laude_ in May, 1973. On August 11, 1973, he married the former Linda Elizabeth Andrews of Lindenhurst, New York. From September 1973 until the present he has been a graduate student in the Quantum Theory Project and the Department of Chemistry at the University of Florida.

The Relyeas have two sons, Matthew Scott and Jonathan Andrew.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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John R. Sabin
Professor of Physics and Chemistry

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Samuel B. Trickey
Professor of Physics

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Martin T. Vala
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Charles P. Luehr
Associate Professor of Mathematics

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June 1980

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Dean, Graduate School